

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
20 March 2003 (20.03.2003)

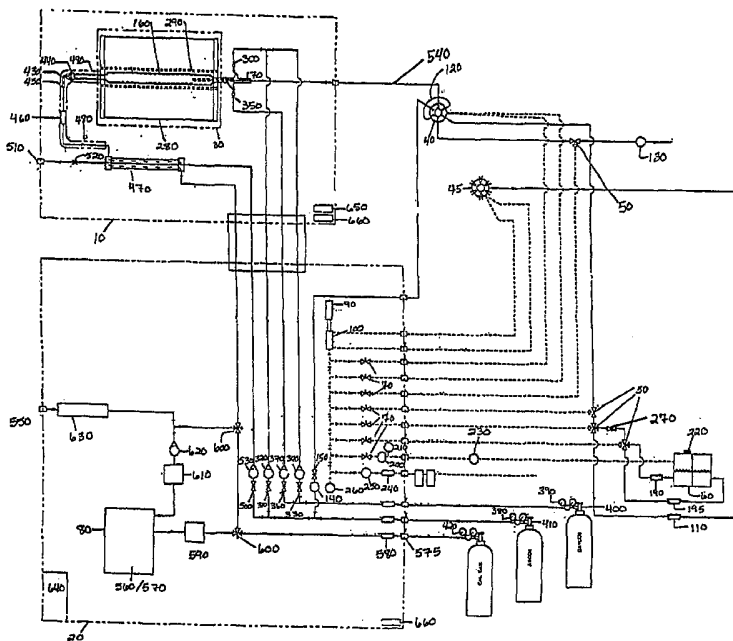
PCT

(10) International Publication Number  
**WO 03/023364 A2**

- (51) International Patent Classification<sup>7</sup>: **G01N** (74) Agent: **BROUGHTON, Avelyn, Ross**; Vinson & Elkins L.L.P., 2300 First City Tower, 1001 Fannin Street, Houston, TX 77002-6760 (US).
- (21) International Application Number: PCT/US02/28967
- (22) International Filing Date:  
11 September 2002 (11.09.2002) (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/951,760 11 September 2001 (11.09.2001) US  
10/055,726 23 January 2002 (23.01.2002) US
- (71) Applicant (*for all designated States except US*): **SPECTRO ANALYTICAL INSTRUMENTS** [US/US]; 1515 North Hwy. 281, Marble Falls, TX 78654 (US).
- (72) Inventor; and (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (75) Inventor/Applicant (*for US only*): **RHODES, John, R.** [US/US]; 8610 Tallwood Drive, Austin, TX 78759 (US).

[Continued on next page]

(54) Title: A METHOD AND APPARATUS FOR THE ON-STREAM ANALYSIS OF TOTAL SULFUR AND/OR NITROGEN IN PETROLEUM PRODUCTS



(57) Abstract: An improved on-stream analyzer for monitoring sulfur or nitrogen content of liquid petroleum or beverage products is described. It consists of the following main components: a sample injector for injecting predetermined fixed volumes of the liquid into a thermal oxidizer (pyrolyzer) at a preset, controlled rate, a thermal oxidizer to thermally oxidize the sample at a temperature of about 1050°C, sample conditioner to control the relative humidity and temperature of the resulting gas mixture, an electrochemical cell sensitive to sulfur dioxide (SO<sub>2</sub>) or NO to measure the concentration of SO<sub>2</sub> or NO in the gas mixture, and a programmable logic controller (PLC) to calculate the sulfur content of the original sample and manage the analyzer. The improved on-stream analyzer may employ additional methods and apparatus for preventing nitrogen interference in the detection of a substance, in particular, new methods and apparatus for preventing interference due to nitrogen in pyro-electrochemical methods. One

preferred apparatus and method comprises a catalytic converter or thermal converter to selectively remove the nitrogen-containing interferant without affecting the sulfur content. A second preferred apparatus and method comprises a chemical scrubber to selectively remove the nitrogen-containing interferant from the gas stream without affecting the sulfur content. Although the analyzer is designed primarily for monitoring sulfur content, it is recognized that the same equipment can be used to analyze any sample having a suitable viscosity and capable of being thermally oxidized under the conditions specified.



**Published:**

— without international search report and to be republished  
upon receipt of that report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**A METHOD AND APPARATUS FOR THE ON-STREAM ANALYSIS OF TOTAL SULFUR  
AND/OR NITROGEN IN PETROLEUM PRODUCTS**

**Field of the Invention**

The present invention relates to new methods and apparatus for the on-stream analysis of total sulfur and/or nitrogen in petroleum products, using a variety of analytical methods, including UV fluorescence, chemiluminescence or electrochemical, in concert with an improved sample injector/injection method and/or an improved dryer/drying method. In addition, it relates to an additional step or feature of an apparatus for preventing nitrogen interference in the detection of a substance. Specifically, it relates to new methods and apparatus for preventing nitrogen interference in pyro-electrochemical methods of analysis if a substance through the selective conversion and/or removal of certain nitrogen-containing interfering gases.

**Background of the Invention**

Sulfur in motor fuels such as gasoline and diesel fuel is an important pollutant. Its concentration has been regulated over the past several years so as not to exceed levels in the range of 500 parts per million (ppm). In order to ensure that the regulated concentration levels are not exceeded, petroleum products are subjected to both laboratory and on-stream analysis during their processing and production. At these concentrations, one of the preferred methods of analysis is x-ray fluorescence spectrometry, described in ASTM methods D 2622 and 4294 incorporated herein by reference, which is well-suited to direct analysis of liquid samples. However, recent government regulations worldwide will reduce the acceptable sulfur contents of gasoline and diesel fuel to below 50 ppm with specific regulatory levels set at 30 and 15 ppm in the next two or three years. It is doubtful whether x-ray fluorescence is sensitive enough to reliably monitor sulfur at 15 ppm, see ASTM Research Report D.02-1456, incorporated herein by reference. Sulfur and nitrogen also occur at parts per million levels in other liquids, such as beverages, and likewise need to be monitored in the ppm range. X-Ray fluorescence is not suitable for measuring nitrogen content.

Suitable methods for use at concentrations down to 10 ppm and below are "pyro-UV fluorescence" (ASTM D 5453) and "pyro-electrochemical" (ASTM D 6428) methods, each method incorporated herein by reference. Nitrogen often occurs in petroleum products and (incidentally) can be measured by "pyro-chemiluminescence" (ASTM D4629) or "pyro-electrochemical" (ASTM D 6366) methods, each method

incorporated herein by reference. In all these methods, a small fixed volume of sample is thermally oxidized ("pyrolyzed") and the combustion products are analyzed for SO<sub>2</sub> or NO. Ultraviolet fluorescence for SO<sub>2</sub> and chemiluminescence for NO both have detection limits of 1 ppb or less, so the sensitivity is good enough to monitor low ppm levels of sulfur or nitrogen in liquids even allowing for the dilution inherent in the pyrolysis step. Similarly, the sensitivity of electrochemical detectors, although not as good as UV fluorescence or chemiluminescence, should be adequate to measure low ppm levels of sulfur and/or nitrogen in liquids, after pyrolysis. Accordingly, the concentrations of these gases may be measured by either UV fluorescence spectrometry (SO<sub>2</sub>), chemiluminescence (NO), or by electrochemical detectors specific for SO<sub>2</sub> or NO. However, electrochemical detectors have the great advantage of simplicity and low cost.

According to the ASTM method directed toward pyro-electrochemical techniques, a fixed volume, usually 5-20 microliters, of liquid sample is injected into the pyrolyzer along with an inert carrier gas, usually argon at a flow rate of about 130-160 sccm (standard cubic centimeters per minute) and including some oxygen, about 10-30 sccm. The liquid vaporizes and then reaches the combustion zone where another flow of oxygen, about 450-500 sccm, the "pyrolysis-gas", is introduced and effects complete thermal oxidation at about 1050° C. The reactor is a quartz tube heated by a tube furnace. The flow rate of liquid sample should never exceed about 4 µl/s (microliters/second), otherwise the combustion process will be starved of oxygen and soot formation (or "sooting") will occur, that is, the internal surfaces downstream of the hot zone will be covered with soot. The ASTM methods specify a flow rate of 1 µl/s. The gas output from the pyrolyzer is a mixture of the inert carrier gas (about 20 vol %), unconsumed oxygen (about 60 vol %), carbon dioxide (CO<sub>2</sub>)(about 10 vol %), water vapor (about 10 vol %) and ppm levels of SO<sub>2</sub> (and ppm levels of oxides of nitrogen, NO and NO<sub>2</sub>, if nitrogen is present in the original sample). The dewpoint is 45-50° C, so the gas lines are usually heat traced and/or the water vapor content is reduced to prevent condensation. Water vapor can be reduced without affecting the SO<sub>2</sub> content by means of a permeation dryer which operates on the principle of absorption-desorption of water vapor through a membrane. The conditioned gas mixture is then fed to the SO<sub>2</sub> detector. A typical 20 µl sample takes some 20 seconds to inject and passes through the pyrolyzer and other gas sample plumbing in about one minute. The SO<sub>2</sub> concentration at the detector starts at zero just before the injection, rises to a maximum and then falls off to

zero. The rates of rise and fall depend on the various flow rates and gas mixing, and on any molecular exchange reactions that the SO<sub>2</sub> undergoes at surfaces with which it comes into contact with. The detector response ideally follows this same profile. The actual detector response will be less than ideal, so additional broadening of the time profile will occur. In practice, the whole SO<sub>2</sub> signal from a given injection will extend over 2-5 minutes. This signal is integrated and is directly proportional to the total amount of sulfur in the original sample. As long as the sample volume remains constant, the SO<sub>2</sub> signal is proportional to sulfur content of the original sample. "Continuous" analysis is accomplished by automating the sample injection procedure.

Known systems for employing these methods, however, have many drawbacks that are avoided by the present disclosure. In particular, known systems fail to guarantee the quality of the pyrolysis, and as a consequence, reproducible and reliable results may not be obtained and sooting may occur. Also, in employing these analysis methods, a dryer is utilized after pyrolysis to insure the quality of the analysis is not adversely affected by the presence of too much water vapor. However, the dryer arrangement employed in known systems is either costly requiring the use of a separate vacuum pump or may fail to prevent the collapse of the sample dryer inner tube.

Moreover, when utilizing an electrochemical detector, the SO<sub>2</sub> sensor, while not sensitive to NO, is highly sensitive to any NO<sub>2</sub> present in the pyrolyzed gas stream, having an NO<sub>2</sub> response equal to upwards of about -100% of the SO<sub>2</sub> response. The pyrolysis occurs in a quartz tube held at about 1050°C in a tube furnace. At this temperature gas chemistry indicates that the thermal equilibrium between the nitrogen combustion products NO and NO<sub>2</sub> is almost completely driven toward about 100% NO, so production of NO<sub>2</sub> is not expected and was not mentioned in any of the relevant ASTM methods.

However, we have surprisingly and unexpectedly found that the SO<sub>2</sub> signal from diesel fuel, for example, containing about 50 ppm nitrogen and about 20 ppm sulfur is strongly suppressed compared to that from diesel containing about 20 ppm sulfur and about zero nitrogen. Part of the sulfur signal is reduced to zero or negative values and the sensor takes as much as one hour to recover after nitrogen is no longer present in the sample. Figure 5 shows a typical effect. It appears that some of the NO is converted to NO<sub>2</sub> in the cooler parts of the pyrolysis tube where the thermal equilibrium favors more

NO<sub>2</sub>. Also, the electrochemical cell appears to be "poisoned" by the NO<sub>2</sub> with long-lasting effects. It is therefore desirable to prevent NO<sub>2</sub> from reaching the SO<sub>2</sub> detector.

The present invention overcomes the drawbacks of known analysis methods by providing reliable and cost-effective on-stream analysis methods and apparatuses for measuring chemical components, including the measurement of total sulfur and nitrogen contents and other components that may be monitored. The present invention accomplishes these objectives by, in certain embodiments, providing reproducible and reliable pyrolysis products and/or by providing an improved dryer design. In addition, the present invention provides a method and apparatus for selectively converting and/or removing interfering gases prior to sample detection. On-stream analyzers preferably operate automatically and reliably and therefore may include many features, components and improvements that enable the erstwhile laboratory method to function successfully as an on-stream analyzer. Such improvements and additional features are described below.

#### **Summary of the Invention**

On-stream analysis for monitoring pollutant levels is of particular importance in many industrial applications. For example the monitoring of sulfur and nitrogen is of concern within the petroleum and beverages industries, however other applications are contemplated by the present disclosure. For simplicity, we refer primarily to monitoring sulfur, although it is contemplated and within the scope of the present invention that the disclosed methods and apparatuses may also be employed for the analysis of other chemical components which may be measured by measuring their pyrolysis products and are capable of detection according to the techniques disclosed herein.

Further, methods and apparatus are described below with special reference to their use in preventing nitrogen interference in laboratory and on-stream sulfur analyzers that employ thermal oxidation, that is pyrolysis, of a sample and electrochemical detection of sulfur-containing species, such as SO<sub>2</sub>. However, the use of such techniques is not limited to this. These techniques can equally be employed to prevent interferences due to other gases, in analyzers for other constituents, such as nitrogen, in laboratory analyzers and on-stream analyzers that use other gas detectors. The methods and apparatus described are, however, limited to analysis techniques that employ thermal oxidation of the sample.

It is therefore an object of the present disclosure to provide reproducible and reliable pyrolysis byproducts for use in an on-stream analyzer by, in certain

embodiments, controlling the volume of a liquid sample dispensed for injection into a pyrolyzer so that it is constant and repeatable. Also, the injection rate is preferably controlled below the upper limit set by "sooting" and above a lower limit below which the analysis takes too long. In practice, there are closer tolerances set not only on the sample injection rate but also on the flow rates of the input gases. If the detector background signal is negligible, the size of the integrated signal, e.g. SO<sub>2</sub> or other chemical signal, would depend only on the total sample volume injected (and its sulfur or other chemical content). Variations in injection rate and in flow rates of the input gases will cause changes in dilution of the SO<sub>2</sub> or other components to be measured in the output gas but this would not matter as long as the total signal were to be integrated. In practice, the background signal is not negligible and the amount of time available to complete the integration is limited, so all of it may not be captured. It follows that the dilution of the SO<sub>2</sub> or other component in the sample is a factor that may preferably be controlled.

Laboratory instruments employ a microliter syringe, usually motorized, to pump a reproducible volume at a reproducible flow rate. This is not practicable in a process analyzer. Instead, the fixed volume sample can be realized by the use of a sample loop and a two-position (two cycle) multiport valve. The loop is filled from the process stream during one valve cycle and emptied into the pyrolyzer during the second cycle. This is described in United States Patent No. 5,152,963 to Wreyford, incorporated herein by reference. However, specific control of the sample injection rate is apparently not described in U.S. Patent No. 5,152,963.

A further object of the present disclosure is to offer an improved means for sample injection rate control. In one embodiment the sample injection rate is controlled as follows: Inert gas, such as argon or helium which is readily available, is introduced at a constant pressure, via a pressure regulator, to a flow restrictor such as a length of capillary tubing, a micro-metering valve (an especially preferred embodiment includes use of a micro-metering valve manufactured by Upchurch Scientific that is capable of being turned down to flow rates of less than 1 µl/s) or an orifice. The gas, thus flowing at a constant rate, pushes the liquid sample out of the fixed volume sample loop, through the injector tube and into the pyrolyzer. Since the volume of sample is fixed, the back pressure produced by it is constant until it begins to flow out of the injector. Then the back pressure goes steadily to near zero. The maximum back pressure is below about

0.4 psi for fuel samples with normal viscosity, about 2 cP (centipoise). The regulated pressure should be in the range 5 to 15 psig, preferably about 8 psi, so the relative change in back pressure is less than 10 % and is repeatable from sample to sample. The flow rate is calibrated prior to operation using a bubblemeter and stopwatch or by timing the appearance and development of the liquid sample drop at the injector tip with the injector out of the pyrolyzer. This assembly provides an injection rate constant to about 10-20 %.

Other methods of controlled injection operate by positive displacement of the liquid sample using a piston. Apart from the abovementioned microliter syringe, operated automatically by a syringe pump or manually, one could employ a piston pump or dispenser such as the FMI Model PiP00SKY. Each of these alternate methods are contemplated by the present invention.

United States Patent No. 5,152,963 and the ASTM methods employ standard laboratory rotometers (floating ball flow meters) with metering valves for flow control of the carrier gas and oxygen. At the flow rates stated above, a 10 % change in each of the input gases will produce the following changes in output sample flow rate and resulting equal changes in SO<sub>2</sub> or NO content through dilution: argon carrier gas, 2 %; oxygen pyrolysis gas, 7 % and oxygen carrier gas, 0.4 %. Errors of this magnitude will show up in the measured sulfur or nitrogen content. An additional object of the present disclosure is to measure each gas flow with an electronic flow meter. The flow data are fed to the Programmable Logic Controller, PLC, and are available to make corrections as necessary to the SO<sub>2</sub> reading. Also contemplated is the use of flow alarms to indicate failure of any gas flow and to greatly reduce the danger of catastrophic equipment failure due, for example, to "sooting". Furthermore, the output gas flow may also be monitored. This enables flow balance calculations to be made with the resulting ability to detect gas leaks, for example. Finally, the quality of the pyrolysis can be checked by monitoring small fluctuations in the output gas flow that occur during pyrolysis.

Other alternate or preferred embodiments of the present disclosure include one or more of the following. (1) The pyrolysis furnace may be enclosed in a sealed container whose outside surface temperature never exceeds 200° C (this is the "surface temperature classification", T3, defined for hazardous locations relevant to our application). Thus, if the enclosure purge fails and the electrical power is consequently cut off, the furnace will



still be at over 1000° C and will take hours to cool down. In a hazardous location, such as an oil refinery, explosive vapors could reach the furnace and cause an explosion even when the electrical power is off. Sealing the furnace is an acceptable method for maintaining equipment safety. (2) A combustible gas sensor may be installed in the enclosure to indicate and provide an alarm for any leak of possibly explosive vapors into this enclosure. (3) The heat trace element for the gas sample stream may comprise a self-limiting cable for extra safety. Such a cable, for example, Omega, Cat# SRL5-2, comprises two parallel conductors separated by a partially conducting polymer. As the temperature increases the resistance between the conductors increases, reducing the heating current. The upper temperature may be limited to about 66° C. (4) The gas sample stream dryer may be operated in a novel manner to avoid problems due to back pressure caused by dryer tube collapse (see detailed description, later). (5) The SO<sub>2</sub> or NO detector may be an electrochemical cell, not a UV fluorescence analyzer. (6) A humidifier may be included just upstream of the electrochemical cell to prevent the relative humidity of the gas falling too low between liquid sample injections, when only dry argon and oxygen are flowing, or when calibration gas is being introduced from a compressed gas cylinder. (7) The relative humidity of the gas sample stream may be monitored and alarm signals available if the relative humidity exceeds a preset upper or lower limit. (8) Liquid sample and calibration sample routing outside the instrument enclosures may be performed by pneumatically operated valves, controlled from within the enclosures, which are intrinsically safe. (9) The calibration liquid samples may be pumped using air or inert gas pressure, also intrinsically safe. (10) The flow rate of calibration liquid may be preset and controlled separately from that of the process fluid in order to conserve expensive calibration liquid and lengthen the time interval required between refilling the calibration reservoirs.

(11) The injector may be mounted so that its tip penetrates the pyrolyzer just far enough to where the pyrolyzer temperature is high enough to smoothly volatilize the liquid sample but not so high as to cause chemical breakdown inside the injector.

One preferred embodiment of the disclosed on-stream analyzer which measures the concentration of a substance in a fluid sample includes a sample injector, a thermal oxidizer, a sample conditioner, a detector, and a programmable logic controller. The sample injector injects the sample at a preset and controlled rate, the sample injector optionally includes a pressure regulator coupled to a flow restrictor, effective to restrict

the flow rate of the sample, thereby slowing, reducing, or eliminating the sample flow. Examples of preferable flow restrictors include a metering valve, a length of capillary tubing having a diameter of about 0.001 to about 0.020 inches, preferably about 0.004 inches, or an orifice with a hole diameter in the range of 0.0005 to 0.005 inches, preferably about 0.002 inches, to control the rate of sample flow. The thermal oxidizer may be enclosed within a container, designed to have an outer surface temperature that does not exceed the lower explosive temperature of the sample being analyzed and to prevent ingress of vapors of the sample being analyzed, and has a tube furnace and a pyrolysis tube, connected to the sample injector so that the sample is injected into the pyrolysis tube, volatilized, and a carrier gas, *i.e.* an inert gas which is preferably argon, helium, or mixtures thereof and optionally containing an admixture of oxygen, and a pyrolysis gas, preferably oxygen, are introduced at a preset, controlled rate, under oxidation conditions. Metering valves are utilized to control the flow rates of the carrier and pyrolysis gases and electronic flowmeters, connected to the programmable logic controller, are employed to measure the flow rates of the carrier and pyrolysis gases as well as the total flow rate of the gas mixture. The electronic flow meters may optionally include an alarm that indicates a flow rate of either carrier or pyrolysis gases that falls outside a preselected range. Oxidation conditions may include a temperature ranging from about 900° C to about 1200° C and preferably about 1050° C. The sample conditioner, connected to and located downstream from the thermal oxidizer, controls the conditions of the resulting gas mixture. The sample conditioner preferably includes one or more of the following, a filter, a dryer, and/or a heat trace element. The filter is preferably made of a chemically inert material, such as polytetrafluorethylene or quartz fiber, and prevents solid particles or liquid drops from passing downstream thereby preventing contamination of downstream components and/or surfaces. The heat trace element is preferably composed of self-limiting electrical heating wires that are effective to maintain the gas stream above its dewpoint from the pyrolysis tube to the dryer. The dryer preferably contains two concentric tubes, an inner tube and an outer tube. The inner tube composed of a membrane for transferring water vapor, preferably the membrane contains active groups for effectuating the water transfer and the active groups are preferably sulfonic acid groups. The outer tube is composed of an inert material that is preferably a fluoropolymer or 316 stainless steel. It is preferable for the dryer to be configured so that a dry purge gas passes through the inner tube and the sample gas is

directed through the annular space between the outer tube and the inner tube. Further, the dryer may optionally contain a restrictor, connected to the inner tube to maintain positive pressure within the dryer. The restrictor preferably includes an orifice having a diameter of about 0.001 inches to about 0.05 inches, preferably 0.0122 inches. The dryer  
5 may optionally include metering valves to control the purge gas flow and electronic flowmeters, connected to the programmable logic controller, to measure the purge gas flow. The electronic flow meters preferably include an alarm to indicate a purge gas flow that falls outside a preselected range. The detector is connected to the sample conditioner and measures the concentration of oxidized substance contained within the  
10 resulting gas mixture. The detector preferably includes an assembly of one or more electrochemical cells where the electrochemical cells are preferably sensitive to SO<sub>2</sub> or NO and may contain an arrangement of electrochemical cells capable of detecting both SO<sub>2</sub> and NO. The programmable logic controller, connected to the detector, calculates the concentration of oxidized substance contained within the gas mixture and  
15 consequently the concentration of substance in the original fluid sample.

Another preferable feature that may be optionally included is a combustible gas sensor to indicate the presence of combustible gas vapors. In addition, it is preferable to utilize a humidifier, located upstream from the detector, to maintain the relative humidity level between about 15 to about 90 %. The humidifier may optionally include a relative  
20 humidity sensor with an alarm to indicate a relative humidity level that falls outside a preselected range.

It is also preferable to utilize non-electric valves to route the fluid sample to the thermal oxidizer, the non-electric valves are preferably pneumatically operated and therefore intrinsically safe. The analyzer also preferably includes a fluid sample outlet  
25 and a non-electric flow indicator to indicate the flow rate of the sample through the fluid sample outlet.

Another optional feature is one or more pneumatic valves for introducing one or more calibration fluids, contained in one or more calibration sample reservoirs (storage vessels), to the injector by means of non-electrical valves, more preferably pneumatically  
30 operated valves. The flow rate of the calibration fluids may optionally be controlled with metering valves. Also, a preferred embodiment may include solenoid valves, controlled by the programmable logic controller, to effectuate flow of the calibration gas directly to the detector, bypassing the thermal oxidizer and sample conditioner. Further,

pneumatically-actuated pressure switches to send signals, via the solenoid valves, to the programmable logic controller to indicate low gas pressure is also preferred.

Another embodiment of the present disclosure involves a method for drying a gas mixture including the steps of providing a gas mixture to be dried, passing a purge gas through an inner tube, feeding the gas mixture through the annular space between the inner tube and an outer tube, restricting the purge gas flow, and capturing the dried gas mixture. The inner tube is comprised of a membrane for transferring water and preferably the membrane contains sulfonic acid groups. The outer tube is comprised of an inert material, preferably a fluoropolymer or 316 stainless steel. It is preferable that the restricting of the purge gas flow is accomplished with a restrictor having an orifice, between about 0.001 to about 0.05 inches in diameter, more preferably 0.0122 inches, to maintain positive pressure.

Another aspect of the present disclosure is to provide for reproducible and reliable laboratory and/or on-stream pyro-electrochemical results by selectively converting and/or removing the interfering gases.

A further preferred feature of the present disclosure is to offer a method and/or apparatus in which the sulfur concentration of the analyzed gas stream is unaffected by the converter. One embodiment prefers that all surfaces "wetted" by the gas stream are inert to sub-parts per million concentrations of  $\text{SO}_2$ , at whatever temperature they must be to perform their function. Some preferred surface materials are composed of stainless steel or quartz. Especially preferred forms of stainless steel include 316 and 304.

Another object of the present disclosure is to keep the pressure drop through the converter minimal, preferably between about zero to about 10 inches of water, so that the quality of the pyrolysis is not deleteriously affected. In addition, pressure fluctuations are preferably kept to a minimum, preferably between about zero to about 10 inches of water, so as not to affect the response of the electrochemical cell.

An additional object of the present disclosure is that the highly enriched oxygen atmosphere of the analyzer gas stream (for example, in one embodiment, about 60%  $\text{O}_2$ , about 20% Ar, about 10%  $\text{CO}_2$  and about 10%  $\text{H}_2\text{O}$ ) preferably does not cause oxidation or combustion of the converter material at the converter operating temperature.

It is a further object of the present disclosure that the nitrogen-containing interferant, for example  $\text{NO}_2$ , is preferably about 100% removed from the analyzed gas stream by conversion to a gas species that does not affect the electrochemical detector,

such as NO. A conversion efficiency of from about 90% to about 100% is preferred and an efficiency of greater than 96% is especially preferred.

5 A further object of the present disclosure is that the equilibrium of the NO<sub>2</sub> to NO reversible reaction (which favors NO<sub>2</sub> at low temperatures) is preferably "frozen" at about 0% to about 10% NO<sub>2</sub> by sufficiently rapid cooling of the analyzed gas stream output from the converter. Cooling the sample gas stream from the converter temperature (in one embodiment about 400°C) to ambient temperature in a period between about 0 to about 10 seconds is preferable and may be achieved by the normal gas flow rate of about 400 to about 800 standard cubic centimeters per minute (sccm) in 10 the 0.25 inch outside diameter by 0.17 to 0.12 inch inside diameter tubing normally used for gas transport.

Another preferred feature of the present disclosure contemplates temperature control of the converter achieved, although not necessarily, by making the converter an integral part of the pyrolysis furnace that provides the pyrolysis temperature.

15 A further object of the present disclosure is that the conversion and/or removal means may be long-lasting, preferably requiring maintenance or replacement at intervals of not less than about one month and preferably of about one year or more.

One preferred embodiment of the present disclosure involves a method for removing nitrogen-containing interferants in pyro-electrochemical methods including the steps of thermally oxidizing a sample containing a substance for detection, for example 20 sulfur-containing species which may be combusted to form SO<sub>2</sub>, selectively removing a nitrogen-containing interferant from the sample gas, for example NO<sub>2</sub>, cooling the sample gas after the selective removal step, and detecting the substance with an electrochemical detector. The selective removal may preferably be accomplished by removing the nitrogen-containing interferant using a scrubber or by selectively 25 converting the nitrogen-containing interferant, for example NO<sub>2</sub>, into a non-interfering species, for example NO. Converters and scrubbers have been used to segregate various gases in instrumentation for air analysis. For example, in chemiluminescence NO<sub>x</sub> analyzers, the chemiluminescent detector measures NO but is not sensitive to NO<sub>2</sub>. A catalytic converter is employed to convert the NO<sub>2</sub> to NO, which it does quantitatively, 30 so enabling the detector to measure NO plus NO<sub>2</sub>, as NO. Stream switching is then employed to alternately bypass the converter, when just NO is measured. The NO<sub>2</sub> content is then calculated by measuring the difference between these values. These

converters function by passing the sample gas stream through a bed of molybdenum, copper or carbon at a controlled temperature in the range 250°C to 400°C depending on the catalyst. A "thermal" converter can also be used which passes the gas through a stainless steel or quartz tube heated to about 900°C, at which temperature the thermal equilibrium between NO and NO<sub>2</sub> is driven towards 100% NO. It is of course important to cool the output gas stream rapidly enough to "freeze" the chemical equilibrium at the 100% NO point achieved in the converter. The use of such converters in NO<sub>x</sub> analyzers does not require the SO<sub>2</sub> content of the gas stream to remain unaffected. Also, it is not known whether the conversion will work effectively in the highly enriched oxygen atmosphere of the pyrolysis exhaust. Another example of a converter is the use of either a heated tube or catalyst bed to convert H<sub>2</sub>S to SO<sub>2</sub>, so that it can be measured by an SO<sub>2</sub> analyzer. A scrubber usually takes the form of a cartridge packed with selected chemicals. Scrubbers are used in air analysis instrumentation to remove unwanted gas species. For example a scrubber may be used to remove SO<sub>2</sub> but leave H<sub>2</sub>S unchanged when an SO<sub>2</sub> analyzer is employed to monitor H<sub>2</sub>S in a gas stream containing both gases. In order to effectively measure H<sub>2</sub>S with an SO<sub>2</sub> detector, an H<sub>2</sub>S to SO<sub>2</sub> converter is necessary. Stream switching is then employed to obtain the separate H<sub>2</sub>S and SO<sub>2</sub> concentrations. Other scrubber chemicals exist that will remove the H<sub>2</sub>S without affecting the SO<sub>2</sub> content. A further example is the use of an ozone scrubber to remove, otherwise toxic, ozone from the exhaust stream of a chemiluminescence NO<sub>x</sub> analyzer. The main advantage of scrubbers is that they almost all operate at room temperature whereas converters require an elevated and/or controlled temperature. On the other hand, scrubbers usually have a limited lifetime as the scrubber chemicals are consumed. Catalytic converters have a theoretically unlimited life which in practice is finite, due to slow poisoning of the catalyst. This selective conversion may preferably be accomplished using a catalyst, a thermal converter or a catalytic converter. Another preferable embodiment contemplates selective removal through combination of a scrubber and converter, either a catalyst, thermal converter, or catalytic converter may be employed as a converter. The catalyst is preferably present in a form where a large surface area is available. Some preferred forms include chips, turnings, wire, foil, screens, and or a series of screens. The catalyst is preferably a Group VIB transition metal, and an especially preferred catalyst is molybdenum. It is further preferable that the pressure drop through the selective removal step is between about 0 to about 10

inches of water, and more preferably less than one inch of water. Another preferred embodiment employs a selective removal step that is effective for removing the nitrogen-containing interferant to about a 90% to about a 100% removal, more preferably about 94% to about 100% removal and most preferably about 96% to about 100% removal. It is additionally preferable for the flow rate of the sample through the selective removal step to be about 400 to about 800 sccm, especially preferable is a flow rate of 650sccm. During the cooling step, it is preferable for the sample to be cooled to ambient temperature within a period of about 0 to about 5 seconds, and more preferably within about 1 second.

Another embodiment of the present disclosure is an apparatus for measuring the concentration of a substance, for example a sulfur-containing species which may be combusted to form  $\text{SO}_2$ , that is effective for preventing interference due to nitrogen-containing interferants, for instance  $\text{NO}_2$ , in pyro-electrochemical techniques. A preferred embodiment includes a thermal oxidizer, where the sample containing a substance for analysis is volatilized under oxidation conditions, a removal device, where the removal device is effective for selectively removing the nitrogen-containing interferant from the sample, and a detector comprising one or more electrochemical cells capable of detecting the substance. The removal device may preferably be a scrubber, a device or material effective for selectively removing the interfering substance from the sample, or a converter, a device or material effective for selectively converting the nitrogen-containing interferant into a non-interfering species. The converter may preferably be a catalyst, a thermal converter, or a catalytic converter. Another preferred removal device utilizes a combination of a scrubber and a converter. The catalyst is preferably present in a form where a large surface area is available. Some preferred forms include chips, turnings, wire, foil, screens, and or a series of screens. The catalyst is preferably a Group VIB transition metal, and an especially preferred catalyst is molybdenum. It is especially preferred, when using chips or turnings, that the converter additionally comprise a catalyst retainer to hold the catalyst materials in place. Preferred catalyst retainers include stainless steel screens, molybdenum screens, quartz wool and permeable quartz plugs. A preferred optional feature of the thermal oxidizer is a temperature control device that is effective for controlling both the temperature of the thermal oxidizer and the removal device. An especially preferred embodiment utilizes a temperature control device to control the temperature of the removal device in an

enclosure separate from that of the thermal oxidizer. A further preferred embodiment contemplates use of both the temperature control device of the thermal oxidizer and the temperature control device of the removal device in tandem to control the temperature of the removal device. An especially preferred feature of the removal device is that it is composed of a material that is inert to the sample gas and is also preferred to be capable of withstanding temperatures of up to about 550°C. The converter preferably operates at a temperature between about 300°C and about 550°C, more preferably between about 350°C to about 450°C, and the scrubber preferably operates at about or near room temperature. Some preferred materials are quartz and stainless steel, especially preferred are 316 stainless steel and 304 stainless steel. It is preferred for the removal device to comprise a housing, where the housing has a first and a second end cap. Some preferred dimensions of the housing include a housing that is about ½ inch outside diameter by about 1/16 inch wall thickness and where the housing is preferably between about 2 to about 6 inches long. The housing preferably includes an input and an output tube for effecting flow of the sample through the removal device. The input and output tubes are preferably about ¼ inch outside diameter by about 0.04 inch wall thickness and are preferably composed of stainless steel. Another preferable feature of the thermal oxidizer is that it is insulated. In addition, it is preferable that the removal device is also insulated. The removal device may preferably be either within the insulation surrounding the thermal oxidizer or contained within a separate insulated environment.

An additional preferred embodiment of the present disclosure contemplates an on-stream analyzer for measuring the concentration of a substance in a fluid sample where the analyzer has a sample injector, a thermal oxidizer, a converter, a sample conditioner, and a detector. It is preferred feature of the sample injector that it is effective for injecting the sample at a preset and controlled rate, and the sample injector may preferably include a pressure regulator coupled to a flow restrictor to control the rate of sample flow. It is preferred that the sample oxidizer include a tube furnace and a pyrolysis tube that is connected to the sample injector. The sample is preferably injected into the pyrolysis tube, volatilized, and mixed with a carrier and a pyrolysis gas, at a preset and controlled rate under oxidation conditions. It is preferred for the converter to selectively convert the nitrogen-containing interferant, such as NO<sub>2</sub>, in the sample to a non-interfering species, like NO, by utilizing a molybdenum catalyst. It is a further preferred feature of the converter to comprise a housing, an input tube, and an output



tube all composed of a material that is inert to the sample gas. Also, it is preferred for the sample conditioner, connected and located downstream from the converter and the thermal oxidizer, to control the conditions of the resulting gas mixture. The sample conditioner may optionally comprise a dryer, for removing water vapor, that has two concentric tubes, an inner tube preferably composed of a membrane capable of transferring water vapor and an outer tube preferably composed of an inert material. In addition, it is preferable for the dryer to be configured so that a dry purge gas flows through the inner tube and the sample gas, to be dried, is directed through the annular space between the inner and outer tubes. The inner tube is preferably connected to a flow restrictor, with an orifice, capable of maintaining positive pressure within the tube. The detector, of the analyzer, may preferably comprise one or more electrochemical cells capable of measuring the concentration of the substance contained within the sample.

Another preferred embodiment of the present disclosure encompasses a method for detecting a substance, for example a sulfur-containing species which may be combusted to form  $\text{SO}_2$ , using pyro-electrochemical analyzer that involves the steps of providing a sample containing a substance for detection in a vapor state, controlling the flow rate of the sample as it progresses through the analyzer, thermally oxidizing the sample, selectively converting the interferant, for example  $\text{NO}_2$ , into a non-interfering species, such as  $\text{NO}$ , cooling the sample, conditioning the sample and detecting the substance. It is preferred for the sample injector to control the flow rate of the sample by utilizing a pressure regulator coupled to a flow restrictor. The use of a catalytic converter having a molybdenum catalyst is preferred to effectuate the selective conversion at about  $300^\circ\text{C}$  to about  $550^\circ\text{C}$ , more preferably between about  $350^\circ\text{C}$  to about  $450^\circ\text{C}$ . It is also preferable for the flow rate of the sample through the converter to be from about 400 sccm to about 800 sccm and preferably have a pressure drop through the converter of less than about 1 inch of water. Another preferred feature of the present disclosure involves a sample conditioning step effective to control the temperature and relative humidity of the sample. The temperature is preferably regulated with a heat trace element comprising self-limiting electrical heating wires and the relative humidity is preferably controlled by a dryer. The preferred embodiment of the dryer comprises two concentric tubes, an inner tube preferably composed of a ion-exchange membrane having sulfonic acid groups and an outer tube preferably composed of a fluoropolymer resin or stainless steel. The dryer is preferably arranged so that the dry purge gas is directed through the inner

tube and the sample gas is directed through the annular space between the inner and outer tube. The inner tube is preferably connected to a flow restrictor having an orifice to maintain positive pressure. The cooling step preferably involves cooling the sample to ambient temperature within a period of about 0 to about 5 seconds and more preferably within about one second. The relative humidity (RH) of the sample reaching the detector is further controlled by means of a humidifier, and monitored by an RH sensor. The sample RH at the detector should be between 15 and 90% and preferably between 40 and 60%. The detection step is preferably accomplished with a detector having one or more electrochemical cells.

Another preferred embodiment of the present invention involves the detection of a substance for detection, for example sulfur-containing species which may be combusted to form SO<sub>2</sub>, either by direct or indirect analysis. Such indirect analysis may be accomplished by detecting a constituent present in the sample to which the substance has been converted and then correlating the amount of that constituent to the amount of the substance prior to conversion.

#### **Brief Description of the Drawings**

Figure 1 is a diagrammatic view of an apparatus according to the disclosure.

Figure 2(a) is a section, to a larger scale, of the sample injection loop configured for an injection cycle.

Figure 2(b) is a section, to a larger scale, of the sample injection loop configured for a flush (loop recharge) cycle.

Figure 3 is a section, to a larger scale, of the dryer configuration.

Figure 3(a) is a section, to a larger scale, of the restrictor configuration.

Figure 4 is a section, to a larger scale, of Enclosure 1.

Figure 5 is a graphical illustration of the typical effects of nitrogen interference.

Figure 6 is a section of a typical converter.

Figure 7 is an illustration of a pyrolysis furnace in combination with a converter.

Figure 8 is a graphical illustration of the typical effects when a converter is used.

Figure 9 is a section of a scrubber.

#### **Detailed Description of the Preferred Embodiments**

Referring to accompanying Figures 1-4, the operation of the sample injector, or "Fast Loop" is first described. For the embodiments analyzing petroleum products, the sample material is likely to be gasoline or diesel fuel and therefore highly flammable. In

those embodiments, no electricity is preferably involved in the valving or pumping outside the instrument enclosures, 10 and 20. For safety, the rotary valves, 40 and 45, and the air valves, 50, are pneumatically operated, and calibration samples are pumped by air or inert gas pressure from the storage vessel, 60. The compressed air or inert gas for this is controlled from within the instrument enclosure by solenoid valves, 70. The process stream sample for analysis is provided under a few psig pressure to rotary valve 40 via valves 45 (optionally), and 50. If several process streams are to be serviced each one may be connected to the multiposition rotary valve, 45, whose position is pneumatically controlled from the main computer (or "PLC"), 80, (note, electrical connections are not shown) via the control modules 90 and 100. The selected process stream flows through filter, 110, to the 6-port, 2-position valve, 40. The pneumatic valves, 50, operated by compressed air or compressed inert gas, are set by solenoid valves, 70, to allow this. The main computer, or Programmable Logic Controller, 80, is programmed to sequence all the solenoid valves in the instrument and control all the functions to be described herein. In the "flush" position of rotary valve, 40, port 1 is connected to port 6 and port 2 to port 3, so that the sample flows through the fixed volume loop, 120, and back to the process via the pneumatic valves, 50, to guard against backflow from the process, and the mechanical flow indicator, 130. The flow indicator is typically a transparent tube, usually glass, with a floating ball, therefore intrinsically safe. Its importance is to show the approximate flow rate of both process fluid and calibration samples and also to indicate the absence of undesirable bubbles in the liquid stream. The 1  $\mu$ l/s, in this example, controlled gas flow from the low pressure regulator, 140, and the micro-metering valve, 150, flows into port 1 of rotary valve, 40, and out of port 5 into the pyrolysis tube, 160. When rotary valve, 40, changes to its "inject" state, ports 1 and 2 are connected together, causing further sample to bypass the valve, while port 4 is connected to port 3 and port 5 to port 6. The gas from micro-metering valve, 150, then delivers the fixed sample volume, in this example 20  $\mu$ l, out of the loop, 120, and through the injector tube, 540, into the pyrolysis tube, 160, via the fitting, 170, at a preset flow rate of, in this example, 1  $\mu$ l/s. Thus a sample of fixed volume is injected at a controlled rate. Typical timing for the two states is preferably about 90 seconds for the injection and about 210 seconds for the flush, giving a total sample measurement cycle time of about 5 minutes, however any suitable timing can be employed.

Calibration samples having known sulfur and/or nitrogen concentrations are stored in the storage vessel, 60. In one embodiment, two concentration levels are stored, although the storage vessel can have any number of compartments, with appropriate valving, to store any number of calibration samples. In normal operation two concentrations may be stored, a high and a low (or zero), to match the upper and lower limits of sulfur or nitrogen content expected in the materials being analyzed. In a calibration cycle, pneumatic valves, 50, are switched by solenoid valves, 70, under PLC control, so as to supply either the "high cal" or the "low cal" sample to rotary valve, 40. Filters 190 and 195 are similar to filter, 110. Calibration sample flow is produced by about 5 to 15 psig of air pressure supplied to the head space in storage vessel, 60, by solenoid valve, 70, and pressure regulator, 200. Pressure switch, 210, sends an alarm signal to the PLC, 80, if the set pressure is too low. Pressure relief valve, 220, prevents any excess pressure build-up in storage vessel, 60. Check valve, 230, prevents any potentially explosive vapors from storage vessel, 60, getting back into the instrument enclosure. Instrument air or inert gas is supplied to power the optional control module, 100, and solenoid valves, 70, via the optional air cleanup cartridges, the filter, 240, and the pressure regulator, 250. The pressure switch, 260, sends an alarm signal to the PLC, 80, if the input instrument air or inert gas pressure is too low. The flow rate of calibration liquid is preset and controlled by metering valve, 270. The calibration samples are close to the injection valve whereas the process stream normally may travel a relatively long distance, possibly tens of feet, to the analyzer. Therefore the flow rate of process stream must generally be much higher than that of the calibration samples in order that the analyzed sample is current. The provision of metering valve, 270, ensures that the calibration sample flow rate can be lower than that of the process stream, so reducing consumption of expensive calibration liquids. Typical flow rates are 40 ccs/min for the process stream and 4 ccs/min for the calibration streams.

Pyrolysis or thermal oxidation of the sample is accomplished as follows. Tube furnace, 280, is operated at 1000 to 1100 degrees C, per the ASTM method. The thermocouple, 290, measures the temperature and sends the signal to the PLC, 80, which controls the temperature. Electrical heater and control wires are not shown. The pyrolysis tube, 160, is a 1 inch diameter by 12 inch long quartz tube (as described in the ASTM method) and may optionally be filled with small quartz tubules (approximately 0.5 inch long by 0.25 inch diameter) designed to increase the surface area available for

the thermal oxidation reactions. Inlet gas, a mixture of argon and oxygen, is introduced through the fitting, 300, from the metering valve, 310, and flow meter, 320, and the valve, 330, and flow meter, 340. Per the ASTM method the argon flow rate is about 150 sccm and the oxygen flow rate about 20 sccm. The valves are manually preset to these rates and the flow meters send their signals to the PLC, 80, which stores and monitors them, alarming if they go out of preset limits. The flow rate signals can also be employed to make corrections to the analysis results. This inlet gas mixture carries the sample, which by the time it reaches the end of the injection tube has vaporized, into the oxidation part of the pyrolysis tube. Pyrolysis gas, a flow of 450 to 500 sccm of oxygen, is introduced at the fitting, 350, and accomplishes complete oxidation of the sample to the products carbon dioxide, water vapor and sulfur dioxide (and oxides of nitrogen, if nitrogen is present). The oxygen flow is controlled by the preset metering valve, 360, and monitored by flowmeter, 370. Argon and oxygen are provided by compressed gas cylinders through two-stage pressure regulators, 380 and 390, respectively. It is well known that the delivery pressures to metering valves must be regulated so that the metering valves can ensure a stable gas flow. The optional pneumatic (therefore intrinsically safe) pressure switches, 400, 410 and 420, send alarm signals to the PLC, 80, if the gas supply pressures fall below acceptable limits. This would usually happen when the compressed gas cylinders are nearly empty and require replacement.

Recognizing that there is a temperature gradient along the axis of the tube furnace from somewhat above ambient temperature at each furnace end wall to the maximum temperature region (1000 to 1200° C, depending on the temperature control setting) in the middle of the furnace, the injector tip must be placed at a distance in the pyrolysis tube from the furnace wall such that its temperature is high enough to cause smooth sample volatilization as it is injected but not so high that the sample is broken down chemically in the inert atmosphere inside the injector tube, causing carbon formation (if the sample is a carbon compound) and consequent injector blockage. A preferable temperature range for the injector tip is from about 400 to about 600° C for diesel fuel samples but the tip can be placed at a point where the temperature is in the range from just above the sample boiling point (diesel boils at temperatures up to about 330° C) to just below the sample breakdown temperature (about 500-600° C for hydrocarbons).

The product of the thermal oxidation is a gas mixture of approximate composition: 60% oxygen, 20% argon, 10% carbon dioxide and 10% water vapor, plus

ppm quantities of sulfur dioxide and, if nitrogen is present in the original process stream, nitric oxide. This flows at a rate of (in this example) 550-650 sccm out of the pyrolysis tube, 160, through the Pyrex socket (elbow), 430 (which is clamped to the tube with a pinch clamp, 440), through the outlet fitting, 450, into the membrane filter, 460. Here any particulates are filtered before the gas flows through the membrane dryer, 470, where the water vapor content is reduced to below the ambient dewpoint. The sample path including tubing and filter holder between the outlet of the pyrolysis tube and the inlet to the Dryer is heat traced, 480, and insulated to maintain a temperature of at least about 50° C (but not exceeding about 66° C) so as to prevent water condensation. The heat trace element, 480, is self-regulating heat trace cable whose temperature should not exceed about 66° C. Thermocouple, 490, is connected to the PLC, 80, that monitors the heat trace temperature and alarms if it goes out of preset limits. The dryer, 470, exchanges water vapor, but none of the other gases present, through its membrane with the dry purge gas that is flowing at a rate of 250-500 sccm on the other side of the membrane. The purge gas in our example is argon, although dry air or other suitable dry gas may be used. The purge gas may be supplied from the argon compressed gas cylinder through the metering valve, 500. The purge gas vents to atmosphere through vent, 510, after passing through the flow restrictor, 520. Flow meter, 530, monitors the flow rate and sends its signal to the PLC, 80, which provides an alarm signal if the flow rate goes outside preset limits.

Drying of the sample gas stream without causing back pressure problems and without resorting to vacuum pumps is accomplished in a novel manner as follows. The dryer, 470, has two concentric tubes, for example, Permapure Model MD-110-24F-4. The inner tube, 475, is composed of a membrane for transferring water vapor that operates on the principle of absorption-desorption and the outer tube, 477, is made of a material that is inert to the sample gases, especially SO<sub>2</sub>, such as 316 stainless steel or a fluoropolymer. One optional embodiment employs perfluoroalkoxy, PFA, for the outer tube. An embodiment for the inner tube may utilize a nonporous membrane that removes gases based upon their chemical affinity for active groups, such as sulfonic acid groups, interspersed within the membrane matrix. One especially preferred embodiment includes a perfluorinated membrane with sulfonic acid groups such as a NAFION membrane. The inner tube is about 0.110 in OD x 0.100 in ID and normally carries the sample to be dried. The outer tube is about 0.250 in OD x 0.190 in ID. The annular space between

the outer and inner tubes normally carries the drying (purge) gas. The inner tube can withstand an internal pressure of at least 100 psig but will collapse if the external pressure on it is greater than the internal pressure by more than about 0.2 psi. This is not a problem in the normal operation mode of these dryers, which is to pull the purge gas through by means of a vacuum pump, in which case the inner tube is always at a greater pressure than the annulus. However, the gases of the claimed invention are introduced at a positive pressure and "pushed" through the system by this pressure. In addition, it is important to have as low a back-pressure as possible at the sample injector tube, 540, to ensure a stable, repeatable injection rate. Therefore all components in the sample gas stream downstream of the injector must be designed for lowest possible pressure drop. The dryer design of the claimed invention prevents collapse of the inner tube while at the same time minimizing sample gas pressure drop by directing the sample gas through the outer annulus while the purge gas is sent through the inner tube at a guaranteed positive pressure. That is, the dryer is operated "inside out". The positive pressure in the inner tube is guaranteed by the restrictor, 520, which is an orifice, 525, with a hole small enough to produce a pressure drop of 1-3psi at the purge gas flow rates used. Such an orifice is available from O'Keefe Controls, Model BS-12-BR, with a hole diameter of 0.0122 in. Orifices with this and other hole diameters of from about 0.001 to about 0.050 inches, depending on the purge gas flow rate, are acceptable for use and available at relatively low cost. The flow restrictor may optionally include a screen, 523, to prevent particles from clogging the orifice. The overall pressure drop of the sample gas from the inlets of the pyrolysis tube, 350, 300 and 170, to the exhaust to atmosphere at 550 is preferably kept at or below about 0.5 psi. The pressure drop across the inner tube membrane should be kept as small as possible so as not to hinder the transport of water vapor molecules across the membrane from the annulus to the inner, dry purge gas. Note that it does not matter in which direction the water vapor molecules travel across the membrane since their transport depends only on the gradient of the water vapor partial pressure. Note also that, since the cross sectional area of the annulus ( $0.122\text{cm}^2$  in our example) is greater than that of the inner tube ( $0.051\text{cm}^2$ ), the pressure drop of the sample gas through the dryer is further reduced from that which it would be if the dryer were operated in its normal mode. Counter flow between the purge and sample gases is preferred but not essential. In this way the driest purge gas first meets the sample gas just before it exits the dryer, ensuring maximum drying efficiency.

The entire sample path between the pyrolysis tube and the SO<sub>2</sub> or NO detector, 560 or 570, preferably comprises a fluorinated polymer or 316 stainless steel wetted parts, to prevent loss or “hang-up” of SO<sub>2</sub> or NO or NO<sub>2</sub> caused by molecular exchange reactions between the SO<sub>2</sub> or NO or NO<sub>2</sub> and any surface it comes into contact with. Condensed water vapor film and any soot particles should be prevented from forming for the same reason.

The SO<sub>2</sub> detector, 560, and optionally NO detector 570, if present, is any suitable electrochemical sensor such as the City Technology Model A3ST/F (for SO<sub>2</sub>) or Model 3NF/F (for NO). The sample gas passing through the sensor preferably has a relative humidity between 15 and 90%. As described above, when thermal oxidation is occurring, the relative humidity is above the dewpoint at ambient temperature so the gas should be dried, which is the purpose of the dryer, 470. However, when the pyrolysis gases argon and oxygen are flowing without a liquid being injected for thermal oxidation, the gases reaching the sensors could be very dry, well below 15% relative humidity. Also, if calibration gas from a compressed gas cylinder is introduced directly to the sensor via 575, 580 and 600, it will have an relative humidity below 15%. Therefore, a humidifier, 590, is included in the sample inlet line to the sensor. This employs a membrane similar to the dryer, except that water is present on the opposite side of the membrane to the sample gas. Water vapor molecules are transported through the membrane to humidify the gas without loss of any SO<sub>2</sub> or NO. By these means the gases reaching the sensors always have a relative humidity between 15 and 90%. The solenoid valves, 600, are switched to send sample or calibration gas through the sensor module, and to bypass sample gas when calibration gas is going through the sensor module. Note that the analysis may be performed by an assembly having more than one sensor of each type, that is an SO<sub>2</sub>-type or NO-type may be incorporated in the sensor assembly. For example, sensors having different sensitivities can be used for monitoring high and low concentration ranges; two or more sensors can be challenged with sample gas in sequence, so as to allow more time for any one sensor to recover to its baseline reading between samples; spare sensors can be mounted and switched into use in the event of sensor failure.

The sample gas leaving the sensor enclosure passes through a relative humidity sensor, 610, and a flow meter, 620, before being scrubbed free of noxious SO<sub>2</sub> and/or NO in the scrubber cartridge, 630, which contains granules of any scrubber material, suitable



for removing SO<sub>2</sub>, NO and excess CO<sub>2</sub>. The cleaned gas is then exhausted to atmosphere through exhaust, 550. The flow rate signal from flowmeter, 620, goes to the PLC, 80, and thereby monitors total sample flow. This is useful for detecting any leaks in the system, since the total of the input flows is also known. Also, the quality of the pyrolysis  
5 "burn" can be monitored since, when the liquid burns it produces an increase in flow rate that matches the temporal burn profile, including fluctuations if the burn is uneven. In addition, absence of pyrolysis when it should be present (an indication of a blocked injector tube or lack of sample, for example) is readily detected.

The instrument enclosures, 10 and 20 are preferably fitted with a standard air or  
10 inert gas purge, 640, to qualify for explosion proof certification. The purge gas is sent to both enclosures (purge plumbing connections not shown). The presence of combustible vapors at or above the Lower Explosive Limit is sensed by, 650, in enclosure, 10, and the signal sent to the PLC, 80, which alarms if vapors are detected. The temperatures of both enclosures are measured by thermocouples, 660, whose signals are monitored by the  
15 PLC, 80, which will alarm if the temperature falls outside the preset limits. Another safety feature is as follows. The pyrolysis furnace is enclosed in a sealed metal container, 30, whose outside surface temperature preferably does not exceed 200° C, the "maximum surface temperature classification", T3, defined for hazardous locations and relevant to our application. An apparatus located in a hazardous location should be  
20 classified according to the maximum surface temperature that can be generated by the instrument either in normal operation or fault condition. This maximum surface temperature should be lower than the ignition temperature of the gas present. The ignition temperatures of gasoline, diesel fuel and kerosene, among the possible samples for analysis under the present invention, are given as 250°, 330° and 210° to 350° C,  
25 respectively. Depending on whether the European or North American standards apply, the maximum surface temperature is divided into 6 or 4 classifications, respectively. In both cases, the relevant classification here is T3, 200° C. The reason for this is if the enclosure, 10, purge fails and the electrical power is consequently cut off, the furnace will still be at a temperature over 1000° C and may take hours to cool down. In use, the  
30 electrically heated center tube of the tube furnace is at the set point temperature (1000° to 1200° C). This tube furnace comprises a tube, surrounded by high temperature insulating fiber, all enclosed in a cylindrical steel can. The surface temperature of the curved part of the steel can is somewhat less than 50° C. The ends of the furnace, on axis, are typically

not insulated, except for the presence of the pyrolysis tube and ceramic end caps to hold the pyrolysis tube clear of the inside surface of the heated tube. Quite a lot of heat escapes from the ends and the surface temperatures range from about 50° C, far from the axis, to about 180° C very close to the axis. Of course, gases can easily penetrate the space between the pyrolysis tube and the furnace tube, which is at about 1000° to about 1200° C and remains well above the ignition temperature of a combustible gas even when the electricity is turned off. A sealed box may prevent ingress of possibly explosive gases in the event of purge failure of the main instrument enclosure, when the electricity would be turned off but the furnace would still be hot. The furnace insulation as well as the air blanket between the furnace and the box keep the surface temperature of the box well below T3 classification. Also, the outer surface of the furnace and the inner surface of the container, 30, should preferably be highly polished to reduce their emissivity and so minimize heat transfer by radiation. In normal operation, the furnace and surface of the enclosed box are kept cool by air or inert purge gas. In the event of purge and power failure cooling may take place by passive means such as convection, conduction and radiation to the surroundings.

There are various methods for processing the detector output to give sulfur content, which will be familiar to anyone experienced in the technology. A typical method is described here. The output signal of the sensor/amplifier subassembly is a voltage assumed to be proportional to SO<sub>2</sub> concentration in the gas passing over the sensor, for a given concentration range, or proportional to NO concentration, if an NO sensor is used. The method to be described assumes the calibration is linear over the range between the upper and lower calibration limits, for example, 0 to 20 ppm or 20 to 40 ppm sulfur in diesel fuel. The sensor signal can be integrated over preset time intervals corresponding to pyrolysis events and also to intervals between pyrolysis events. The “gross signal” can be integrated (electrical circuitry is not shown in Flow Diagram) over a preset time interval corresponding to the sensor response to the pyrolysis event. The “background signal”, defined as the output during some interval between pyrolysis events, may also be integrated and stored. After suitable normalization for possibly different integration intervals and optional averaging over a preselected number of pyrolysis events, the background signal is subtracted from the gross signal to give the “net signal”. This integral, I, is converted to sulfur concentration, C, by the following equation.

$$C = aI + b$$

Where a and b are calibration constants:

$$a = (C_h - C_l) / (I_h - I_l)$$

5

$$b = C_h - aI_h$$

The calibration is valid only between the two concentrations  $C_h$  and  $C_l$ , which are the sulfur contents of the high and low calibration samples, respectively, giving the net signals  $I_h$  and  $I_l$ , respectively.

10

In certain circumstances conversion must be made between ppm by weight and ppm by volume. The sample is delivered for injection in aliquots of constant volume (the sample loop volume). If a weight/volume result is required (e.g., grams per liter or grams per gallon) and the standards are quoted in terms of the same units of wt/vol, no density correction between standards and unknowns is needed. However, if a wt/wt result is required (e.g., g/g) and the standards are quoted in terms of wt/wt, a density correction must be made to both standards and unknowns:

15

$$(gS/g)_{unk} = (\text{density of std} / \text{density of unknown}) \times (gS/g)_{std}$$

If a wt/vol result is required and the standards are quoted in terms of wt/wt, only the standards need to be corrected for density:

20

$$(gS/ml)_{unk} = (\text{density of std, g/ml}) \times (gS/g)_{std}$$

If a wt/wt result is required and the standards are quoted in term of wt/vol, only the unknowns need to be corrected for their density:

25

$$(gS/g)_{unk} = (1 / \text{density of unknowns}) \times (g/ml)_{std}$$

Figures 5-9 illustrate another aspect of the present invention. Figure 5 shows the results of measuring successive 20 microliter injections of diesel fuel, injected

into the Pyrolysis Tube at 5 minute intervals and measured with an electrochemical SO<sub>2</sub> sensor. The area under each peak (and also the peak height since the peak shapes are similar to each other) is proportional to the sulfur signal. The first 5 injections, designated 701 through 705, are of a sample containing 20 ppm sulfur and zero nitrogen. It is seen that the sulfur signal is stable and repeatable. Between the fifth, 705, and sixth, 706, injections, the sample is changed to one containing 20 ppm sulfur and 50 ppm nitrogen. The sulfur signal is immediately reduced and part of it goes to zero and may be driven negative, injections #6 to #11, at 706 to 711. The effect becomes steadily worse even though the nitrogen content is constant. Between injection #8, 708, and #9, 709, the sample is switched back to 20 ppm sulfur with zero nitrogen. It is seen that it takes about 7 more injections, designated by 710 through 716, before the sensor fully recovers from the effects of the nitrogen.

An especially preferred converter type is catalytic because the temperature required is much lower than other methods and is within the range obtainable by burying the converter cartridge inside the pyrolysis furnace insulation. The preferred catalyst material is a Group VIB transition metal and more preferably molybdenum, which is known to operate well in the temperature range 300-550°C. Molybdenum is especially preferred because it is less likely to be oxidized by the enriched oxygen atmosphere of the pyrolysis exhaust than either copper or carbon, other potential catalysts and is less likely to react with SO<sub>2</sub>.

Figure 6 shows a sketch of a typical converter. It is preferable for the materials wetted by the sample gas, to be unreactive to SO<sub>2</sub> and capable of withstanding at least about 550°C. One preferred embodiment employs stainless steel or quartz. The pressure drop across the whole cartridge at the preferred sample flow rates of about 400 to about 800 sccm (standard cubic centimeters per minute) is preferably so small that extra back-pressure does not affect the quality of the pyrolysis upstream and any pressure fluctuations are preferably so small as to not affect the response of the electrochemical sensor downstream. One preferred embodiment aims for a pressure drop of less than about 1 inch of water at a gas flow of about 650 sccm. In another embodiment, the housing, 720, is about ½ inch outside diameter by 1/16 inch wall thickness stainless steel tubing 2 to 6 inches long. The end-caps, 725, are stainless steel Swagelok reducing unions, catalog number SS-810-6-4 (or equal). The input and output tubes, 730, are about ¼ inch outside diameter by about 0.040 inch wall thickness stainless steel tubing.

The catalyst filling, 735, is either molybdenum wire, foil, mesh, screen, chips or turnings, or a series of molybdenum screens wedged in place, and preferably having suitable spacer rings. It is preferable that the chip size range or screen mesh size and spacing be selected so as to provide maximum surface area to the flowing gas without excessive pressure drop. The catalyst retainers, 740, preferred where the filling, 735, is chips or turnings, consist of stainless steel or molybdenum screens wedged into place between the housing ends, 745, and the unions, 750. It is preferable that the catalyst filling be such as to prevent "channeling" of the sample gas, for example, by settling of the chips to leave a gap (if the orientation of the converter is horizontal).

All materials wetted by the gas are preferably clean to avoid adsorption of  $\text{SO}_2$  by, for example, oil films. A suitable cleaning process is to rinse in 1:1 HCl, then de-ionized water, then methanol, and allow to air dry at room temperature.

The converter is preferably placed inside the pyrolysis furnace, buried in the insulation at a location where the temperature is between about 300°C and about 550°C. A typical commercially available tube furnace is about 8 inches outside diameter by about 12 inches long, with the center hole, on axis, about 1.5 inches in diameter. The heater is preferably coiled around the center hole and is controlled at about 1050°C to provide this temperature along at least some of the length, for the pyrolysis tube that goes in the hole. The space between the heater coils and the outside enclosure is filled with ceramic fiber insulation.

Figure 7 shows a cylindrical pyrolysis tube furnace illustrating two preferred placements for the converter, at positions labeled 795 and 810. Item 755 is the cylindrical furnace outer casing; 760 is the quartz pyrolysis tube which is placed in the furnace tube; 765 is the ceramic fiber furnace insulation that fills the space between the furnace tube and the outer casing; 770 is the carrier gas inlet (in one preferred embodiment argon plus oxygen); 775 is the pyrolysis gas inlet (in one preferred embodiment, oxygen); 780 is the sample injector port, the sample injector port is connected to a sample injector that preferably injects the sample at a preset and controlled rate, a particularly preferred embodiment of the present disclosure utilizes a pressure regulator coupled to a flow restrictor to control the sample flow; 785 is the pyrolysis tube filling of small quartz tubules; 790 represents the pyrolysis temperature zone where the temperature is in the range of about 1000°C to about 1050°C; 800 is a particulate filter to prevent any soot or other particles from the pyrolysis migrating

downstream; and may optionally include a sample conditioner, located downstream of the converter, where the sample conditioner preferably contains a dryer.

One preferred embodiment of the present disclosure utilizes a pressure regulator coupled to a flow restrictor to effectuate injection of the sample at a preset and controlled rate. In one preferred embodiment the sample injection rate is controlled by introducing an inert gas, such as argon or helium, at a constant pressure, via a pressure regulator, to a flow restrictor such as a length of capillary tubing, a micro-metering valve or an orifice. The gas, thus flowing at a constant rate, pushes the liquid sample out of a fixed volume sample loop or other sample measuring device, through an injector tube and into the pyrolyzer. When using a length of capillary tubing, a diameter between about 0.001 to about 0.020 inches is preferable. Another especially preferred embodiment of the flow restrictor employs a micro-metering valve capable of flow rates of less than 1  $\mu\text{l/s}$ . The flow rate may be calibrated prior to operation using a bubblemeter and stopwatch or by timing the appearance and development of the liquid sample drop at the injector tip with the injector out of the pyrolyzer. Another preferred embodiment employs an orifice, that is a hole in a plate through which a fluid is forced to flow, having a hole diameter of about 0.0005 to 0.005 inches.

The critical flow rate for a fluid through an orifice is the rate which is required when that fluid is forced to flow at the speed of sound. For a gas, as the ratio,  $R$ , of downstream to upstream pressure is decreased the flow rate increases until the critical pressure ratio,  $R_c$ , is reached where the flow velocity is equal to the speed of sound for the gas. At this point, further decreases in this pressure ratio,  $R$ , do not increase the flow rate through the orifice. There are many practical applications of this phenomenon, including flow measurement and control. The critical flow rate for a gas is reached when  $R_c$  equals about 0.5, the precise value depending on the atomicity of the gas. For example  $R_c$  for air or oxygen is 0.53 and that for argon or helium is 0.49. The critical volume flow rate,  $q$ , for a gas is given by the formula:  $q = (cd^2P\sqrt{T})/M$ , where  $c$  is a constant,  $d$  is the orifice diameter,  $P$  is the upstream pressure,  $T$  is the absolute temperature and  $M$  is the gas molecular weight. For argon flowing at 1  $\text{l/s}$ , the orifice diameter must be about 2 microns.

Good long term stability can be achieved by manufacturing the orifice from suitable materials and by ensuring that blockages do not occur. A suitable material for this application is stainless steel, though any material chemically compatible with the gas

flowing through the orifice, the ambient conditions and the need to make the orifice plate thin, is suitable. To prevent blockages, it is preferable to include a filter capable of filtering out particles down to less than the orifice diameter (and preferably less than about one fifth of the orifice diameter) in the gas flow immediately upstream of the orifice. Preferably, a stainless steel frit (item 28) with 0.2 micron porosity, although any suitable filter known to those familiar with the science of filtering, is employed. The critical orifice flow rate is inherently independent of downstream pressure, so errors due to backpressure variations will not occur. The upstream pressure, P, must be controlled and this is preferably done by inclusion of the pressure regulator. Since the downstream pressure is atmospheric to within 1 or 2 psig, (that is, in absolute terms, about 14 to 16 psia at sea level) the upstream pressure must exceed about  $16/0.49$ , or about 33 psia, which is about 18 psig, for critical flow of argon. (Psig = pounds per square inch gauge. Pounds per square inch absolute (psia) equals psig plus atmospheric pressure which at sea level is 14.7 psia). Thus the pressure regulator is set at about 20 psig, to regulate down the pressure output from the gas cylinder which is set at about 30 psig. In fact, it is not necessary to include the regulator if the gas cylinder regulator can be reliably set at a controlled pressure that is greater than 18 psig. Referring to the above critical flow equation, it is seen that changes in critical flow rate are directly proportional to changes in absolute upstream pressure. Therefore, control of this absolute pressure to within 5% or better of its set value, for example  $20 \pm 1$  psig, will ensure that flow rate changes due to pressure changes will be 5% or less. Most commercially available pressure regulators are much more precise than this. It is preferable that actual pressure setting is not so high as to force the use of an orifice smaller than one micron diameter which is not currently available. This sets a practical upper limit to the regulated pressure of about 66 psia, or 51 psig. A further advantage of the pressure regulator is that it can be employed to "tune" the flow rate to precisely what is required. In practice, the critical orifice (a critical orifice refers to an orifice with a diameter small enough such that it is practicable to achieve a critical flow rate of a sample as disclosed herein) diameter cannot be made to exact tolerances although it can be made within a range of, say  $\pm 25\%$  of 2 microns (for example), which would yield the required flow rate to within  $\pm 50\%$  since the flow rate depends on the square of the diameter. The ability to tune the flow rate to more precise tolerances is clearly of practical importance. Temperature effects are minimal, since the critical flow rate depends on the square root of the absolute temperature. At an

ambient temperature of about 300K a 10°C rise in temperature takes the absolute temperature to 310K, a relative change of 3.3%. since the flow velocity varies as the square root of absolute temperature, the corresponding relative change in critical orifice flow rate is only about  $(3.3/2)\%$ , or about 1.7%.

5           It should be noted that any or all of the metering valves may be replaced by critical orifices, if the corresponding flow rates never need adjustment. The following nominal orifice diameters will give the required critical flow rates when the upstream pressure is regulated to 28 psig: 160 sccm of inlet (carrier) argon, 87 microns; 400 sccm of dryer purge argon, 138 microns; 20 sccm of inlet oxygen, 29 microns; and 475 sccm  
10 of pyrolysis oxygen, 142 microns.

Notwithstanding the abovementioned explanation for the critical orifice, the use of such an orifice in a non-critical flow mode is also feasible and often advantageous. The only difference is that the independence from downstream pressure variations is lost. Non-critical flow rates, lower than critical flow rates, are obtained when the upstream  
15 pressure is lower than that required for critical flow. In the present context any upstream pressure between about 8 and 18psig would give suitable flow rates. Eight psig is the practical lower limit where sensitivity to downstream pressure variations becomes too great, as described above. Above 18psig the flow for argon is critical. The ability to tune the flow rate by changing the pressure regulator setting is an important practical  
20 advantage that sometimes offsets the increased sensitivity to downstream pressure fluctuations

A further preferred embodiment makes use of a sample conditioner connected to and located downstream from the pyrolysis furnace and the converter. The sample conditioner controls the conditions of the resulting gas mixture. The sample conditioner  
25 preferably includes one or more of the following, a filter, a dryer, and/or a heat trace element. The filter is preferably made of a chemically inert material, such as polytetrafluorethylene or metal screen, preferably stainless steel, and prevents solid particles or liquid drops from passing downstream thereby preventing contamination of downstream components and/or surfaces. The heat trace element is preferably composed  
30 of self-limiting electrical heating wires that are effective to maintain the gas stream above its dewpoint from the pyrolysis tube to the dryer. The dryer preferably contains two concentric tubes, an inner tube and an outer tube. The inner tube composed of a membrane for transferring water vapor, preferably the membrane contains active groups



for effectuating the water transfer and the active groups are preferably sulfonic acid groups interspersed within the membrane. One preferable embodiment includes a perfluorinated membrane with sulfonic acid groups such as a NAFION membrane. The outer tube is composed of an inert material that is preferably a fluoropolymer or stainless steel. It is further preferable for the dryer to be configured so that a dry purge gas passes through the inner tube and the sample gas is directed through the annular space between the outer tube and the inner tube. Further, the dryer may optionally contain a restrictor, connected to the inner tube to maintain positive pressure within the dryer. The restrictor preferably includes an orifice having a diameter of about 0.001 inches to about 0.05 inches, preferably 0.0122 inches.

Item 810 is one preferred zone for placement of the converter material, where the temperature range is between about 300°C to 550°C. This embodiment achieves a preferred temperature by placing the converter at about ½ to about 1 inch inside the outer wall of the furnace enclosure, on a horizontal radius out from the heater coil and centrally located axially. Item 805 is the inlet and outlet tubing to this embodiment of the converter, and comprises stainless steel or quartz; 810 is the converter; 820 is the converter filling; 825 is the sample gas outlet to the sample dryer and detector subassemblies and other components as necessary (such as a programmable logic controller for calculating data obtained from the detector) for the on-line pyro-electrochemical analyzer; 830 is the furnace thermocouple used for furnace temperature sensing, control and alarming; 835 is the converter thermocouple used for sensing, control and alarming the converter temperature; 840 is the electrical heater for the pyrolysis tube furnace; and 845 is the electrical heater for the converter cartridge. Another preferred placement is shown in the exhaust portion of the quartz pyrolysis tube, 795, where the temperature is in the proper range, between about 300°C to about 550°C. In this case, the converter material, 815, is preferably molybdenum wire, suitably coiled to provide maximum surface area to the gases and minimum pressure drop.

Note that the catalytic converter may also be housed in a separate temperature-controlled, insulated enclosure.

Performance tests of this converter are shown in Figure 8, where samples containing 20 ppm sulfur and either zero or 50 ppm nitrogen were analyzed, just as in Figure 1. As before, successive 20 microliter injections of sample into the pyrolysis tube are made at 5-minute intervals, designated by numbers 850 through 861. The height of

each signal peak is proportional to the electrochemical sulfur dioxide signal. The first three injections, 850 through 852, are of 20 ppm sulfur, zero ppm nitrogen in diesel fuel and are made without the converter installed. The converter is then installed between the third, 852, and fourth, 853, injections. The signal does not change, indicating that the SO<sub>2</sub> content is unaffected by the converter. The sample is changed to 20 ppm sulfur, 50 ppm nitrogen between injections #5, 854, and #6, 855. The sulfur signal remains unchanged (except for some instability caused by the experimental procedure). The sample is then changed back to 20 ppm sulfur, zero nitrogen between injections #9, 858, and #10, 859. Again the sulfur signal is essentially unaffected. It is seen that the sulfur signal remains steady both before and after the converter is installed, and with or without 50 ppm nitrogen in the samples. This verifies a) that NO<sub>2</sub> is being produced during or immediately after pyrolysis, b) that the converter does not react significantly with SO<sub>2</sub>, c) that the molybdenum converter is converting a significant portion of NO<sub>2</sub> back to NO and d) that the chemical reaction is effectively "frozen" after the gases exit the converter.

Preferably, the scrubber effectively removes the NO<sub>2</sub> from the sample while not affecting the SO<sub>2</sub> concentration and preferably operates at or near room temperature. It is also preferable that the active chemical of the scrubber not react significantly with any other gas present, such as the O<sub>2</sub>, CO<sub>2</sub> or water vapor. If water vapor affects the scrubber chemical, it is preferable for the scrubber to be located downstream of the dryer, which is already present as a preferred embodiment of the pyro-electrochemical analyzer.

Selection of a chemical that satisfies the criteria of reacting with NO<sub>2</sub> yet being inert to other gases in the stream, especially SO<sub>2</sub>, may be difficult. There are numerous chemicals that satisfy the criteria set forth herein, the selection of which is within the skill of one in the art, and each are contemplated by the present disclosure.

Figure 9 shows a sketch of a typical scrubber cartridge. Pressure drop requirements are the same as for the converter cartridge, although the scrubber is preferably designed to operate at or near room temperature. In one embodiment, the housing, 865, is preferably about ½ inch outside diameter by about 1/16 inch wall thickness, composed of a fluoropolymer, for example "TEFLON", or stainless steel tubing 2 to 6 inches long. The end-caps, 870, are preferably stainless steel or a fluoropolymer reducing unions. The input and output tubes, 875, are preferably about ¼ inch outside diameter by about 1/16 inch wall thickness and composed of a fluoropolymer or stainless steel tubing. The filling, 885, preferably consists of the active

chemical deposited from solution on an inert support, is preferably porous, and preferably has a large surface area. Some preferred support materials include turnings or shavings of porous fluorcarbon polymer, or pieces of fluorcarbon membrane filter. The filling is preferably packed so as to prevent channeling, to preferably provide maximum surface area to the flowing gas stream and to preferably avoid excessive pressure drop. The retaining plugs, 880, are preferred where the filling requires them, and are preferably quartz wool although any suitable inert, porous material may be utilized. All materials wetted by the gas are preferably clean so as to avoid any adsorption of SO<sub>2</sub> by, for example, oil films. A suitable cleaning process for the tubing and fittings is to wipe with methanol and allow to air dry at room temperature.

What is claimed is:

1. An on-stream analyzer for measuring the concentration of a substance in a fluid sample, said analyzer comprising:
  - a. a sample injector for injecting the sample at a preset and controlled rate, the sample injector further comprising a pressure regulator coupled to a flow restrictor to control the rate of sample flow;
  - b. a thermal oxidizer comprising a tube furnace and a pyrolysis tube, connected to the sample injector, wherein the sample is injected into the pyrolysis tube, volatilized, and a carrier gas and a pyrolysis gas are introduced, at a preset, controlled rate, to the sample under oxidation conditions;
  - c. a sample conditioner, connected to and located downstream from the thermal oxidizer, to control the conditions of a resulting gas mixture;
  - d. a detector, connected to the sample conditioner, to measure the concentration of oxidized substance contained within the gas mixture; and
  - e. a programmable logic controller, connected to the detector, to calculate the concentration of oxidized substance contained within the gas mixture and consequently the concentration of substance in the original fluid sample.
2. The analyzer of claim 1 further wherein the flow restrictor is a metering valve.
3. The analyzer of claim 1 wherein the flow restrictor is a length of capillary tubing having a diameter of from about 0.001 to about 0.020 inches.
4. The analyzer of claim 1 wherein the flow restrictor is an orifice.
5. The analyzer of claim 4 wherein the orifice has a diameter of about 0.0005 to about 0.005 inches.
6. The analyzer of claim 4 wherein the rate of sample flow through the orifice is about 1  $\mu\text{l/sec}$ .

7. The analyzer of claim 4 wherein the rate of sample flow through the orifice is greater than or equal to the critical flow rate.
8. The analyzer of claim 4 wherein the rate of sample flow through the orifice is less than the critical flow rate.
- 5 9. The analyzer of claim 1 further comprising a container to enclose the thermal oxidizer.
- 10 10. The analyzer of claim 1 further comprising one or more electronic flowmeters to measure the flow rates of carrier and pyrolysis gases introduced, and the total flow rate of the gas mixture.
- 11 11. The analyzer of claim 10, further comprising metering valves for controlling the flow rates of the carrier and pyrolysis gases.
- 12 12. The analyzer of claim 10 wherein the electronic flowmeters are connected to the programmable logic controller.
- 15 13. The analyzer of claim 10 wherein the electronic flowmeter further comprises a gas flow alarm to indicate a flow rate of carrier gas, pyrolysis gas, or gas mixture that falls outside a preselected range.
- 14 14. The analyzer of claim 1 wherein the oxidation conditions include a temperature range of from about 900° C to about 1200° C.
- 20 15. The analyzer of claim 1 wherein the detector comprises an assembly having one or more electrochemical cells.
- 16 16. The analyzer of claim 15 wherein one or more electrochemical cells measures the concentration of SO<sub>2</sub> in the mixture.
- 17 17. The analyzer of claim 15 wherein one or more electrochemical cells measures the concentration of NO in the mixture.
- 25 18. The analyzer of claim 15 wherein the one or more electrochemical cells further comprises an electrochemical cell capable of detecting SO<sub>2</sub> and an electrochemical cell capable of detecting NO.

19. The analyzer of claim 15 further comprising a removal device, located up-stream from the detector, for selectively removing a nitrogen-containing interferant from the sample.
20. The analyzer of claim 19 wherein the removal device is a scrubber.
- 5 21. The analyzer of claim 19 wherein the removal device selectively converts the nitrogen-containing interferant into a non-interfering species.
22. The analyzer of claim 19 wherein the removal device comprises a scrubber and a converter.
- 10 23. The analyzer of claim 1 further comprising a combustible gas sensor to indicate the presence of combustible gas vapors.
24. The analyzer of claim 15 further comprising a humidifier located upstream from the assembly having one or more electrochemical cells.
25. The analyzer of claim 24 wherein the humidifier operates to maintain a relative humidity level of about 15 to 90 %.
- 15 26. The analyzer of claim 24 wherein the humidifier comprises an alarm to indicate a relative humidity level which falls outside a preselected range.
27. The analyzer of claim 1 wherein the sample conditioner comprises a filter, a dryer and a heat trace element, the heat trace element further comprising self-limiting electrical heating wires effective to maintain the gas stream temperature above its dewpoint from the pyrolysis tube to the dryer.
- 20 28. The analyzer of claim 27 wherein the filter is a chemically inert membrane designed to prevent solid particles or liquid from passing downstream without significantly restricting the gas flow.
- 25 29. The analyzer of claim 1, further comprising a fluid sample outlet stream and a non-electric flow indicator to indicate the flow rate of the fluid sample outlet stream.

30. The analyzer of claim 1, further comprising one or more valves for introducing one or more calibration fluids, contained in one or more calibration sample reservoirs, to the injector.
- 5 31. The analyzer of claim 1, further comprising solenoid valves controlled by the programmable logic controller to effectuate flow of a calibration gas directly to the detector, bypassing the thermal oxidizer and sample conditioner.
32. The analyzer of claim 1, further comprising solenoid valves and pneumatically-actuated pressure switches to send signals via solenoid valves to the programmable logic controller to indicate low gas pressure.
- 10 33. The analyzer of claim 30, further comprising one or more metering valves to control the flow rate of the calibration fluids.
34. The analyzer of claim 27 wherein the dryer comprises two concentric tubes, an inner tube composed of a membrane for transferring water vapor and an outer tube composed of inert material, wherein the dryer is configured to operate so that a dry purge gas is directed through the inner tube and the sample gas is directed through the annular space between the inner and outer tube, and further wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure.
- 15 35. The analyzer of claim 34 wherein the inert material is a fluoropolymer or stainless steel.
- 20 36. The analyzer of claim 34 wherein the membrane is a membrane having sulfonic acid groups.
37. The analyzer of claim 34 wherein the orifice has a diameter of about 0.001 to about 0.05 inches.
- 25 38. The analyzer of claim 34 further comprising a metering valve to control the purge gas flow.
39. The analyzer of claim 38 further comprising an electronic flow meter, connected to the programmable logic controller, to monitor the purge gas flow.

40. The analyzer of claim 39 wherein the electronic flow meter further comprises an alarm to indicate a purge gas flow that falls outside a preselected range.

41. An on-stream analyzer for detecting a substance in a fluid sample, said analyzer comprising:

5 a. a fluid sample injector for injecting a sample at a preset and controlled rate;

b. a thermal oxidizer, connected to the sample injector, wherein the sample is injected into the thermal oxidizer and a carrier gas and a pyrolysis gas are introduced to the sample under oxidation conditions;

10 c. a sample conditioner, connected to the thermal oxidizer, to control the conditions of a resulting mixture, wherein the conditioner further comprises a dryer for removing water vapor, wherein the dryer further comprises two concentric tubes, an inner tube composed of a membrane for transferring water vapor and an outer tube composed of an inert material, wherein the dryer is configured to operate so that a dry purge gas is directed through the inner tube and the sample gas is directed through the annular space between the inner and outer tube, and further wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure;

15 d. a detector, connected to the sample conditioner, to measure the concentration of oxidized substance contained within the gas mixture; and

20 e. a programmable logic controller, connected to the detector, to calculate the concentration of a substance contained within the mixture.

25 42. The analyzer of claim 41 wherein the sample injector further comprises a pressure regulator coupled to a metering valve to control the rate of sample flow.

43. The analyzer of claim 41 wherein the sample injector further comprises a pressure regulator coupled to a length of capillary tubing having a diameter of from about 0.001 to about 0.020 inches to control the rate of sample flow.



44. The analyzer of claim 41 wherein the sample injector further comprises a pressure regulator coupled to an orifice to control the rate of sample flow.
45. The analyzer of claim 41 wherein the inert material is a fluoropolymer or stainless steel.
- 5 46. The analyzer of claim 41 wherein the membrane is a membrane having sulfonic acid groups.
47. The analyzer of claim 41 wherein the detector comprises an assembly having one or more electrochemical cells.
- 10 48. The analyzer of claim 41 further comprising a removal device, located up-stream from the detector, for selectively removing a nitrogen-containing interferant from the sample.
49. The analyzer of claim 48, wherein the removal device is a scrubber.
50. The analyzer of claim 48, wherein the removal device selectively converts the nitrogen-containing interferant into a non-interfering species.
- 15 51. The analyzer of claim 48, wherein the removal device comprises a scrubber and a converter.
52. An apparatus for measuring the concentration of a substance in a sample and effective in removing nitrogen interference in pyro-electrochemical methods comprising:
- 20 a. a thermal oxidizer;
- b. a removal device for selectively removing the nitrogen-containing interferant from the sample; and
- c. a detector, wherein the detector comprises an assembly of one or more electrochemical cells capable of detecting the substance.
- 25 53. The apparatus of claim 52, wherein the removal device is a scrubber.

54. The apparatus of claim 52, wherein the removal device selectively converts the nitrogen-containing interferant into a non-interfering species.
55. The apparatus of claim 54, wherein the removal device is a thermal converter.
56. The apparatus of claim 54, wherein the removal device comprises a catalyst.
- 5 57. The apparatus of claim 56, wherein the removal device is a catalytic converter.
58. The apparatus of claim 52, wherein the removal device comprises a scrubber and a converter.
59. The apparatus of claim 56, wherein the catalyst is Group VIB transition metal.
- 10 60. The apparatus of claim 56, wherein the catalyst is operative in the range of about 300°C to about 550°C.
61. The apparatus of claim 52 wherein the thermal oxidizer additionally comprises a temperature control device, the temperature control device being effective for controlling the temperature of the removal device.
62. The apparatus of claim 52 wherein the removal device additionally comprises a temperature control device.
- 15 63. The apparatus of claim 61 wherein the removal device additionally comprises a separate temperature control device.
64. The apparatus of claim 52 wherein the removal device is composed of a material that is inert to the sample.
- 20 65. The apparatus of claim 64 wherein the material is capable of withstanding temperatures of up to about 550°C.
66. The apparatus of claim 52 wherein the removal device is located in a temperature controlled enclosure separate from that of the thermal oxidizer.
- 25 67. The apparatus of claim 52 further comprising a sample injector for injecting the sample, at a preset and controlled rate, into the thermal oxidizer, wherein said

sample injector further comprises a pressure regulator coupled to a flow restrictor.

- 5                   68.    The apparatus of claim 52 further comprising a sample conditioner, connected to and located downstream from the thermal oxidizer, to control the conditions of the sample, wherein the conditioner further comprises a dryer, wherein the dryer comprises two concentric tubes, an inner tube composed of a membrane for transferring water vapor and an outer tube composed of inert material, wherein the dryer is configured to operate so that a dry purge gas is directed through the inner tube and the sample gas is directed through the annular space between the inner and outer tube, and further wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure.
- 10
69.    A method for detecting a substance in a sample comprising the steps of:
- a.     providing a sample in vapor state;
- b.     thermally oxidizing the sample;
- 15                  c.     conditioning the oxidized gas mixture to control the temperature and relative humidity, wherein the temperature is regulated with a heat trace element comprising self-limiting electrical heating wires and wherein the relative humidity is controlled by a dryer comprising two concentric tubes, an inner tube composed of a membrane having sulfonic acid groups and an outer tube composed of a fluoropolymer resin or stainless steel, wherein a dry purge gas is directed through the inner tube and the sample gas is directed through the annular space between the inner and outer tube, and further wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure;
- 20
- d.     passing the gas mixture through a detector effective to detect a substance; and
- 25                  e.     processing the detector output.

70. The method of claim 69 comprising the additional step of controlling the rate at which the sample progresses by using a pressure regulator coupled to a flow restrictor.
71. The method of claim 70 wherein the flow restrictor is an orifice.
- 5 72. The method of claim 71 wherein the sample flow rate through the orifice is independent of the downstream pressure.
73. The method of claim 71 wherein the sample flow rate through the orifice is equal to or greater than the critical flow rate.
- 10 74. The method of claim 71 wherein the sample flow rate through the orifice is less than the critical flow rate.
75. The method of claim 71 wherein the sample flow rate through the orifice is 1 $\mu$ l/sec.
76. The method of claim 69 comprising the additional step of selectively removing a nitrogen-containing interferant from the sample.
- 15 77. The method of claim 76 wherein the selective removal step comprises converting the nitrogen-containing interferant into a non-interfering species.
78. A method for detecting a substance in a sample comprising the steps of:
- a. providing a sample in vapor state;
- b. controlling the rate at which the sample progresses by using a pressure  
20 regulator coupled to a flow restrictor;
- c. thermally oxidizing the sample;
- d. passing the resulting gas mixture through a detector effective to detect a substance; and
- e. processing the detector output.

- 5 79. The method of claim 78 further comprising the additional step of exposing the oxidized gas mixture to a dryer to remove water vapor from the oxidized gas mixture, wherein the dryer comprises two concentric tubes, an inner tube composed of a membrane for transferring water vapor and an outer tube composed of inert material, wherein the dryer is configured to operate so that a dry purge gas is directed through the inner tube and the sample gas is directed through the annular space between the inner and outer tube, and further wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure.
- 10 80. The method of claim 78 comprising the additional step of selectively removing a nitrogen-containing interferant from the sample.
81. The method of claim 80 wherein the selective removal step comprises converting the nitrogen-containing interferant into a non-interfering species.
- 15 82. A method for drying a flowing gas mixture comprising the steps of:
- a. providing a flowing gas mixture to be dried;
- b. passing a purge gas through an inner tube;
- c. feeding the gas mixture through the annular space between the inner tube and an outer tube;
- 20 d. restricting the purge gas flow with a restrictor having an orifice, between about 0.001 to about 0.05 inches in diameter, to maintain positive pressure; and
- e. capturing the dried gas mixture.
83. The method of claim 82 wherein the inner tube is a membrane for transferring water vapor.
- 25 84. The method of claim 83 wherein the membrane is a membrane having sulfonic acid groups.

85. The method claim of 82 wherein the outer tube is a fluoropolymer resin or stainless steel.
86. The method of claim 82 wherein the orifice has a diameter of about 0.0122 inches.
- 5 87. A method for removing nitrogen interference in pyro-electrochemical methods of analysis, the method comprising the steps of:
- a. thermally oxidizing a sample to produce a sample gas;
  - b. selectively removing a nitrogen-containing interferant from the sample gas;
  - 10 c. cooling the sample gas; and
  - d. detecting the substance with an electrochemical detector.
88. The method of claim 87 wherein the selective removal is accomplished by using a scrubber.
89. The method of claim 87 wherein the selective removal step comprises selectively  
15 converting the nitrogen-containing interferant into a non-interfering species.
90. The method of claim 87 wherein the nitrogen-containing interferant is NO<sub>2</sub> and further wherein the NO<sub>2</sub> is selectively converted to NO.
91. The method of claim 89 wherein the selective conversion step is accomplished by using a catalyst.
- 20 92. The method of claim 91 wherein the catalyst is present in a catalytic converter.
93. The method of claim 89 wherein the selective conversion step is accomplished by using a thermal converter.
94. The method of claim 89 further comprising a second selective removal step accomplished by using a scrubber.
- 25 95. The method of claim 91 wherein the catalyst is Group VIB transition metal.
96. The method of claim 91 wherein the catalyst operates in the range of about 300°C to about 550°C.

- 5           97.     The method of claim 87 wherein the detected substance is a sulfur-containing species.
98.     The method of claim 97 wherein the detected substance is SO<sub>2</sub>.
99.     The method of claim 87 wherein the pressure drop through the selective removal  
step is between about 0 to about 10 inches of water.
100.    The method of claim 99 wherein the pressure drop through the selective removal  
step is less than 1 inch of water.
101.    The method of claim 87 wherein the selective removal of the nitrogen-containing  
interferant is from about 90% to about 100% conversion.
- 10          102.    The method of claim 87 wherein the sample is cooled to ambient temperature  
within a period of about 0 to about 5 seconds.
103.    The method of claim 89 wherein the thermal oxidation is accomplished using a  
pyrolysis furnace, and where the pyrolysis furnace is effective to control the  
temperature of the selective conversion step.
- 15          104.    The method of claim 87 wherein the flow rate of the sample through the  
selective removal step is about 400 to about 800 sccm.
105.    The method of claim 87 comprising the additional step of controlling the rate at  
which the sample progresses by using a pressure regulator coupled to a flow  
restrictor.
- 20          106.    The method of claim 87 comprising the additional step of conditioning the  
sample to control the temperature and relative humidity, wherein the temperature  
is regulated with a heat trace element comprising self-limiting electrical heating  
wires and wherein the relative humidity is controlled by a dryer comprising two  
concentric tubes, an inner tube composed of a membrane having sulfonic acid  
25          groups and an outer tube composed of a fluoropolymer resin or stainless steel,  
wherein a dry purge gas is directed through the inner tube and the sample gas is  
directed through the annular space between the inner and outer tube, and further

wherein the inner tube is connected to a flow restrictor having an orifice to maintain positive pressure.



Figure 1

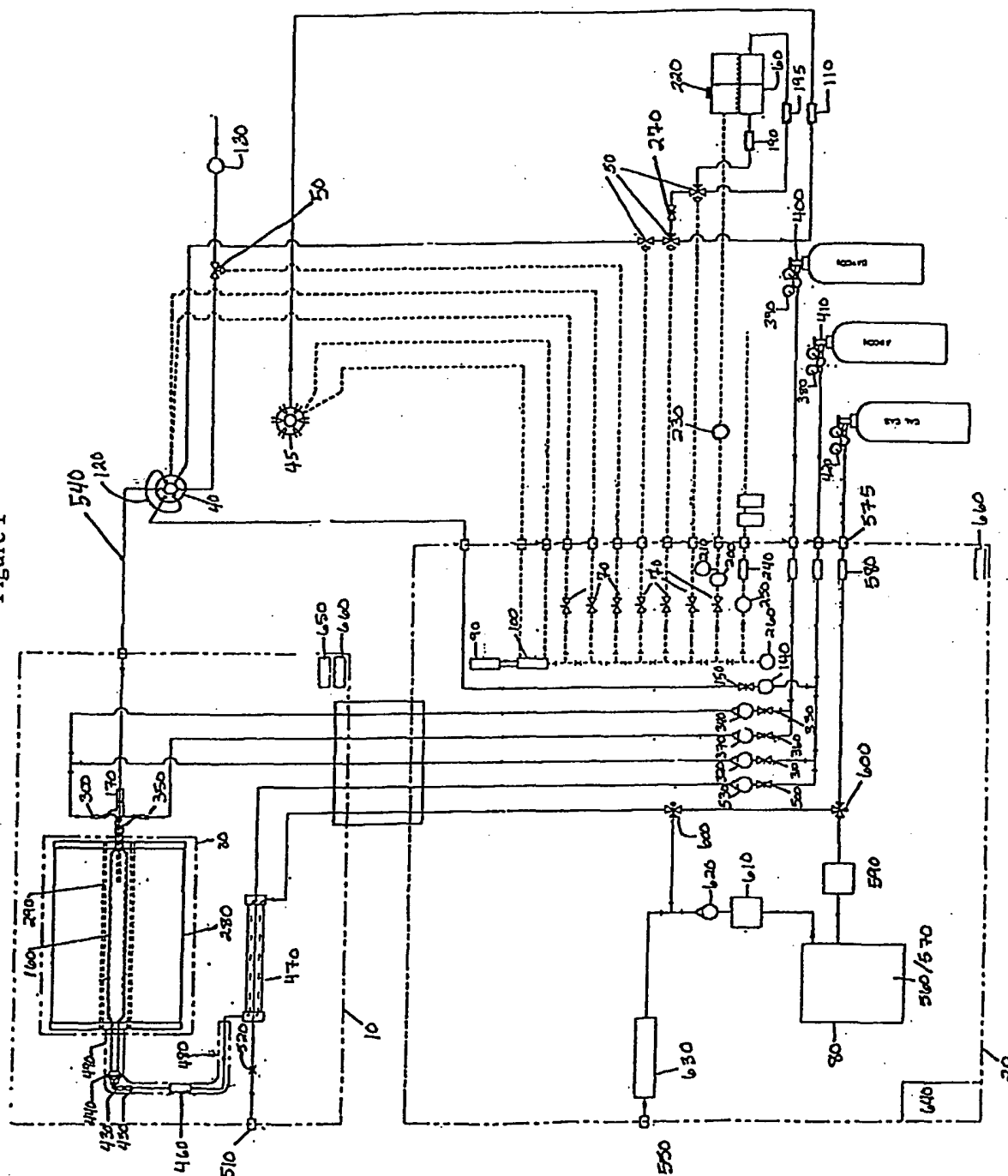
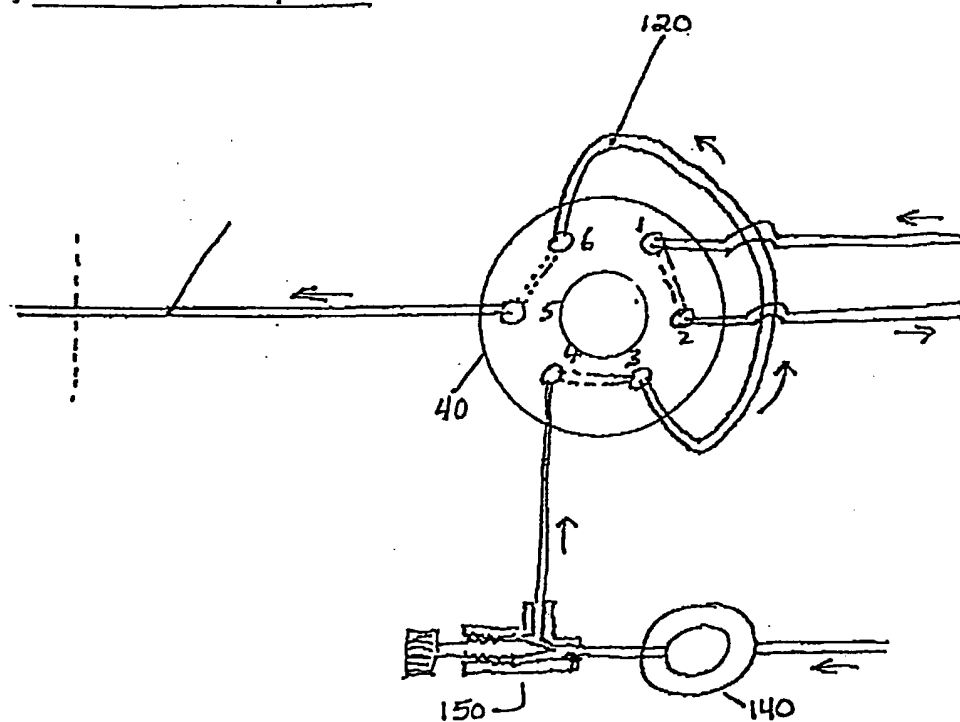


Figure 2

SAMPLE INJECTION LOOP SHOWING THE  
PRESET AND CONTROLLED RATE

a) INJECTION CYCLE



b) FLUSH (LOOP RECHARGE) CYCLE

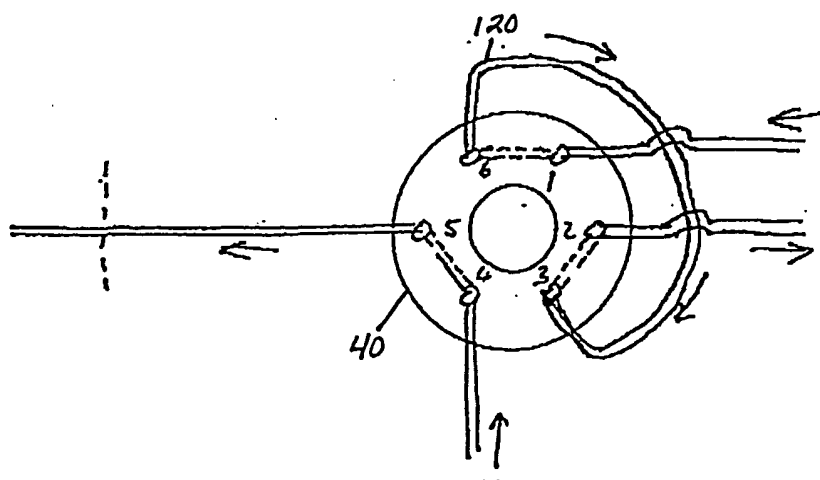
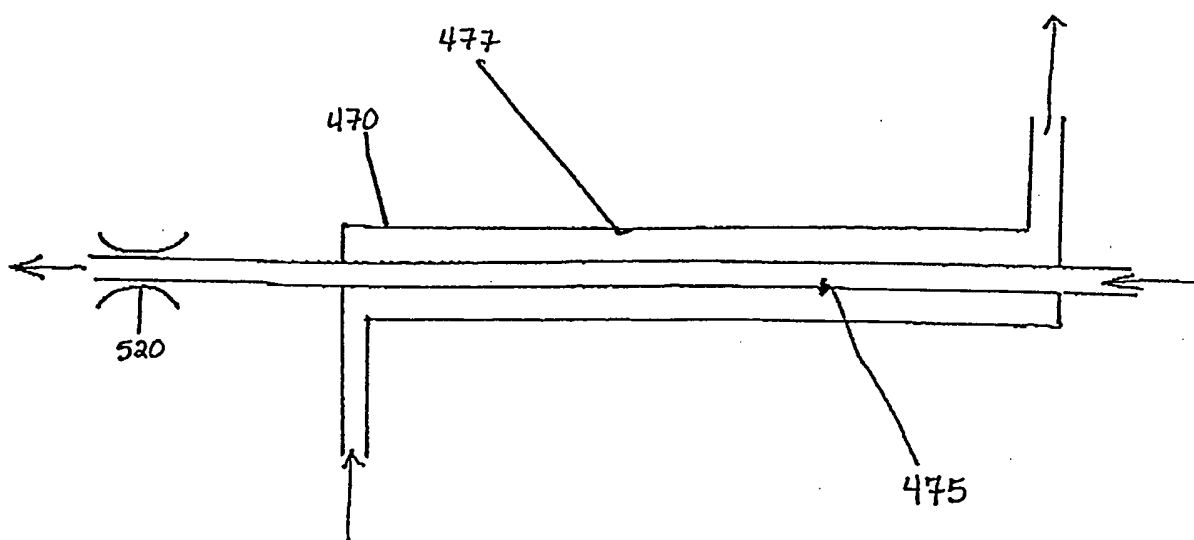


Figure 3  
DRYER CONFIGURATION



3(a) DETAIL OF ORIFICE-TYPE RESTRICTOR

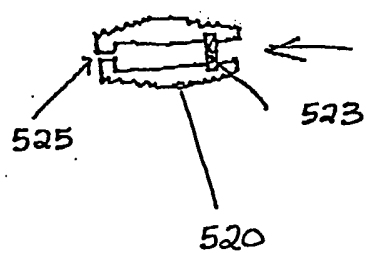


Figure 4

290

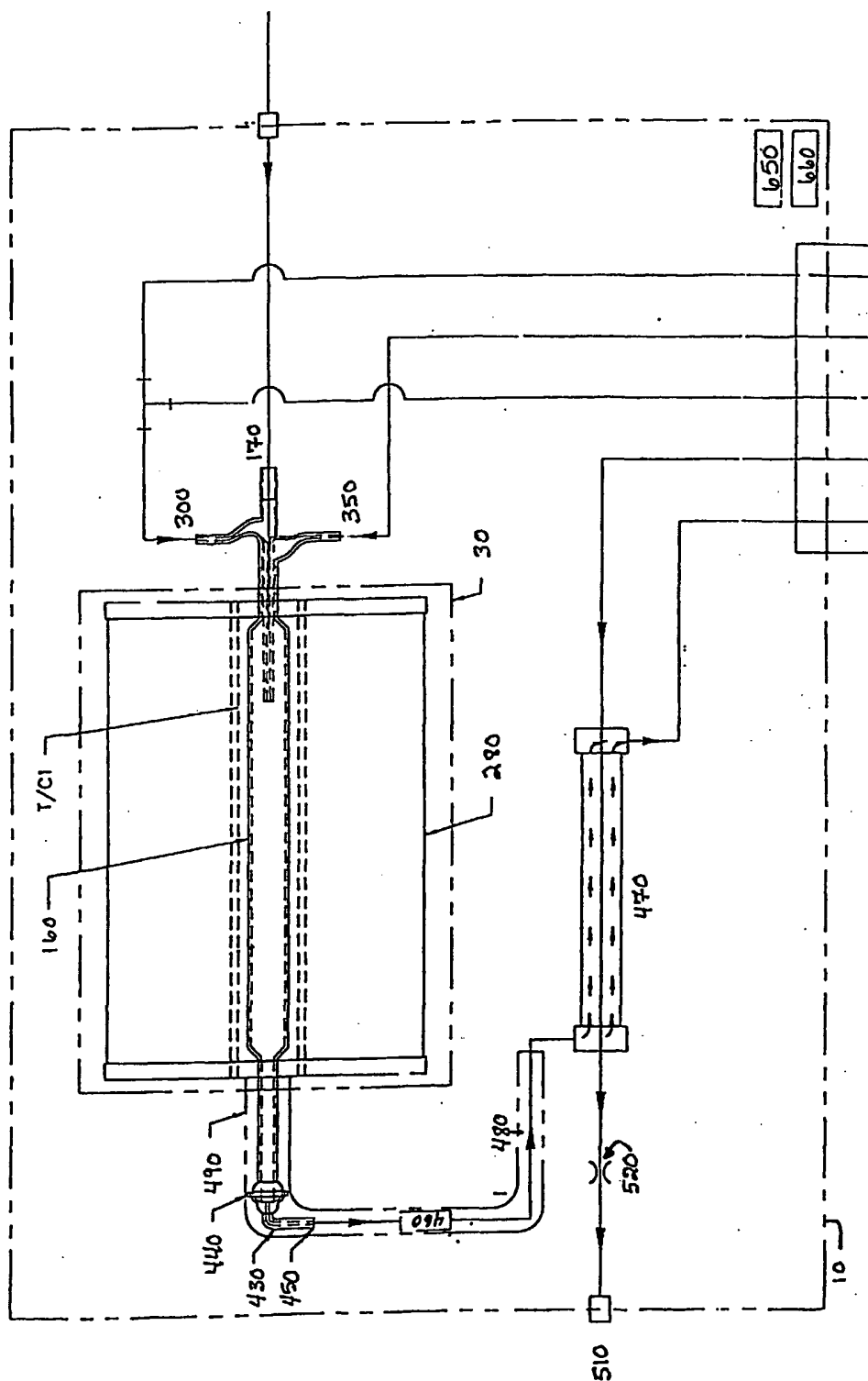


FIGURE 5

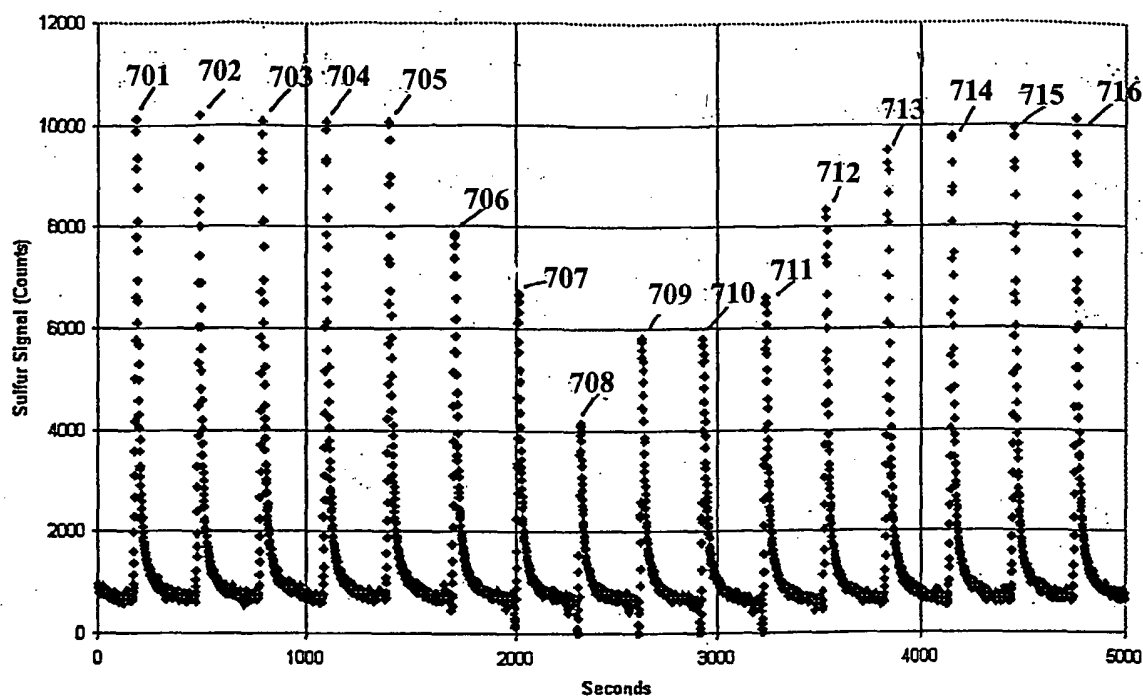


FIGURE 6

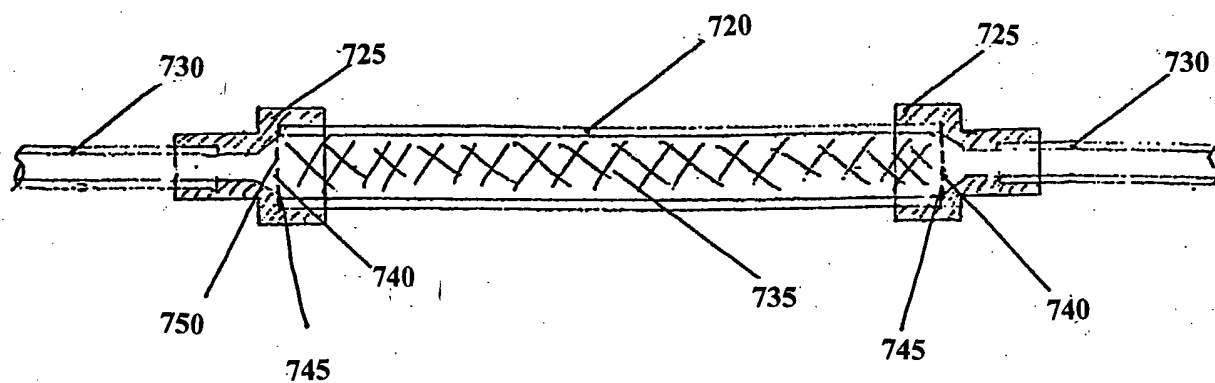


FIGURE 7

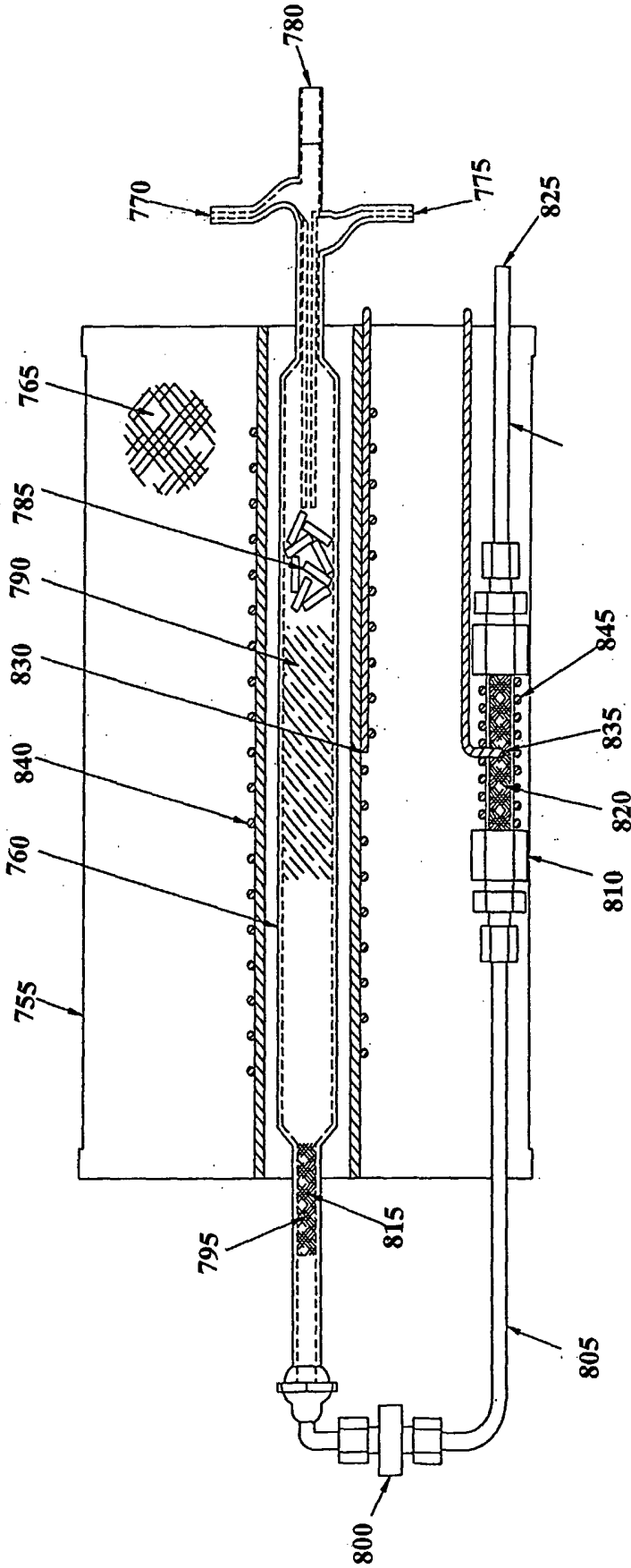


FIGURE 8

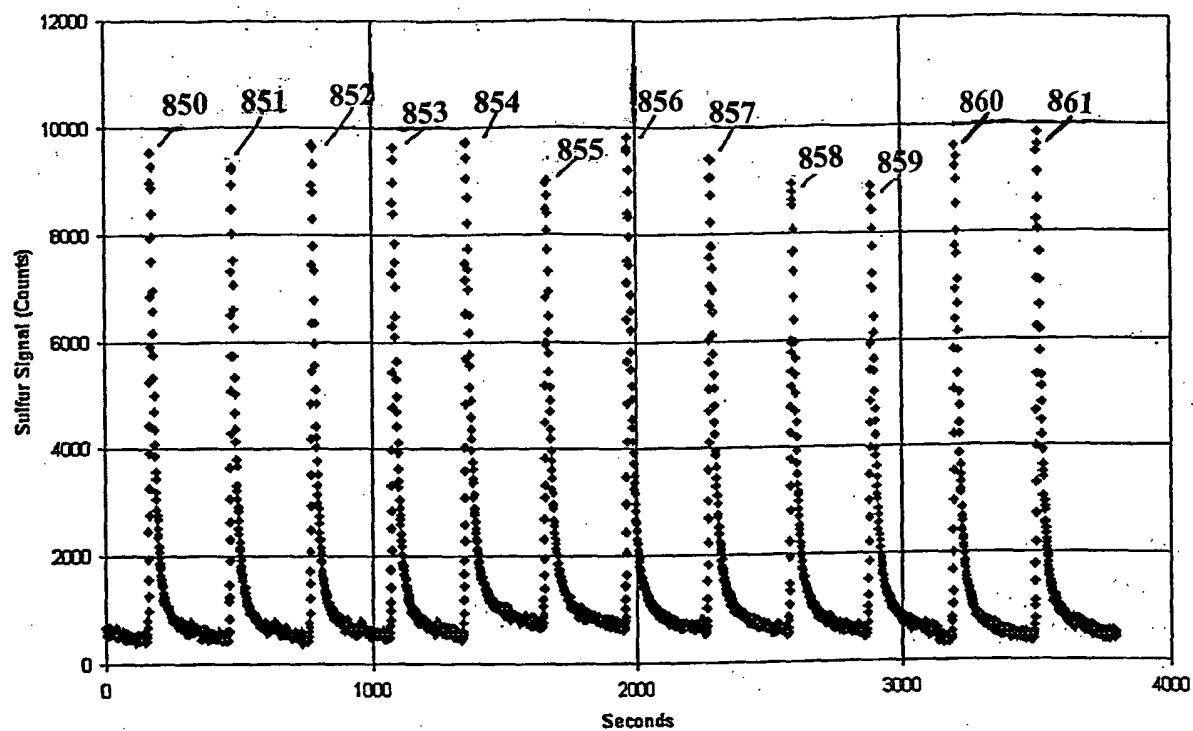




FIGURE 9

