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<b>(21) International Application Number:</b> PCT/US94/01590 <b>(22) International Filing Date:</b> 18 February 1994 (18.02.94)  <b>(30) Priority Data:</b> 08/020,804      22 February 1993 (22.02.93)      US  <b>(71) Applicant:</b> THE COCA-COLA COMPANY [US/US]; 310 North Avenue, Atlanta, GA 30313 (US).  <b>(72) Inventors:</b> ROUNBEHLER, David, R.; 276 Great Road, Bedford, MA 01730 (US). FINE, David, H.; 4 Whispering Pine, Sudbury, MA 01776 (US). MACDONALD, Stephen, J.; 17 Norwood Road, Salem, NH 03079 (US). DENNISON, Daniel, B.; 3207 DBD Frey Lake Road, Kennesaw, GA 30144 (US). ACHTER, Eugene, K.; 18 Mason Street, Lexington, MA 02173 (US).  <b>(74) Agents:</b> BIRCH, Anthony, L. et al.; Birch, Stewart, Kolasch & Birch, P.O. Box 747, Falls Church, VA 22040-0747 (US).		<b>(81) Designated States:</b> AU, BR, CA, HU, JP, KP, NO, PL, PT, RO, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A METHOD AND SYSTEM FOR SAMPLING AND DETERMINING THE PRESENCE OF COMPOUNDS  <b>(57) Abstract</b> <p>A system and method are provided for minimizing the effects of background signals in masking signals indicating the presence of substances to be detected such as contaminants in materials moving rapidly along a conveyor. The contaminants detected may include nitrogen containing compounds and hydrocarbons. The system and method of the present invention minimize during detection of the presence or absence of such substances, the number of falsely positive indications of the presence of such substances due to background signals and changes in background signals. The substances detected are divided into first and second sample portions and the respective portions are heated. The first heated portion is mixed with ozone to cause a chemical action therewith in order to generate radiation by chemiluminescence having characteristic wavelengths related to substances in the first portion. The second portion heated is also mixed with ozone to cause a chemical reaction therewith in order to generate radiation by chemiluminescence having characteristic wavelengths related to substances in the second portion. The radiation of the respective first and second portions is selectively detected. The heating and detecting steps are performed in a manner so as to yield a higher level of detected radiation from one of the portions of the sample than the other for at least some of the selected compounds being detected. Electrical signals from the respective first and second portions are generated and compared in order to determine the presence or absence of selected compounds in the sample. Appropriate reject signals for a bottle sorting system are generated accordingly.</p>		

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A METHOD AND SYSTEM FOR SAMPLING AND DETERMINING  
THE PRESENCE OF COMPOUNDS

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of application Serial Nos. 07/890,863 filed June 1, 1992 and 07/890,864 filed June 1, 1992, both of which are assigned to  
5 the same assignee as the present invention.

The present invention relates to an inspection system for sampling and determining the presence of certain substances, such as residues of contaminants within containers such as glass or plastic bottles. More  
10 specifically, the present invention relates to an improved sampling and analyzing system and method for determining the presence of substances such as residues of contaminants, as in containers such as beverage bottles rapidly moving along a conveyor past a test station in a container sorting system.

15 In many industries, including the beverage industry, products are packaged in containers which are returned after use, washed and refilled. Typically refillable containers, such as beverage bottles, are made of glass which can be easily cleaned. These containers are washed and then  
20 inspected for the presence of foreign matter.

Glass containers have the disadvantage of being fragile and, in larger volumes, of being relatively heavy. Accordingly, it is highly desirable to use plastic containers

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because they are less fragile and lighter than glass containers of the same volume. However, plastic materials tend to absorb a variety of organic compounds which may later be desorbed into the product thereby potentially adversely affecting the quality of the product packaged in the container. Examples of such organic compounds are nitrogen containing compounds such as ammonia, organic nitrogen compounds, and hydrocarbons including gasoline and various cleaning fluids.

10 The aforementioned application Serial No. 07/890,863 discloses a system and method for detecting the presence of these nitrogen containing and hydrocarbon compounds using a chemiluminescence analyzer. That system and method works quite well, but improvements are desirable to overcome  
15 interferences which may occasionally cause difficulties in achieving desired sensitivity and accuracy of detection. Such interferences result from background signals which may mask detection of low levels of certain compounds and whose variation with time may also result in false positives (and  
20 thus unwarranted rejection of uncontaminated containers). Accordingly, a need in the art exists for a chemiluminescence analyzer with improved accuracy and sensitivity.

#### SUMMARY OF THE INVENTION

Accordingly, it is a primary object of the present  
25 invention to provide a method and system for detecting the presence or absence of specific substances - e.g., contaminants such as nitrogen containing compounds and hydrocarbons, in materials as the materials move rapidly along a conveyor with improved accuracy which minimizes the  
30 deleterious effects of background signals.

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It is a particular object of the invention to minimize the effects of background signals in masking signals indicating the presence of such substances to be detected.

It is another particular object of the invention to  
5 minimize, during detection of the presence or absence of such substances, the number of falsely positive indications of the presence of such substances due to background signals and changes in background signals.

The objects of the present invention are fulfilled by  
10 providing a method comprising the steps of:

collecting a sample;

dividing the sample into first and second portions;

heating the first portion of the sample to a first  
temperature;

15 heating the second portion of the sample to a second  
temperature;

mixing the heated first portion of the sample with ozone  
to cause a chemical reaction therewith in order to generate  
radiation by chemiluminescence having characteristic  
20 wavelengths related to substances in said first portion;

mixing the heated second portion of the sample with  
ozone to cause a chemical reaction therewith in order to  
generate radiation by chemiluminescence having characteristic  
wavelengths related to substances in said second portion;

25 selectively detecting radiation emitted by  
chemiluminescence from the first portion of the sample;

selectively detecting radiation emitted by  
chemiluminescence from the second portion of the sample;

said heating and detecting steps being performed in a  
30 manner so as to yield a higher level of detected radiation  
from one of said portions of the sample than the other for at  
least some of the selected compounds;

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generating first electrical signals from the radiation selectively detected from the first portion of the sample and second electrical signals from the radiation selectively detected from the second portion of the sample; and

- 5        comparing the first electrical signals with the second electrical signals in order to determine the presence or absence of selected compounds in the sample;

          said heating, mixing, detecting, and generating, steps for said first portion being performed at essentially the  
10 same time as said heating, mixing, detecting, and generating steps for said second portion, and said comparing step being performed in a manner so as to cancel background signals in said portions.

          In a preferred embodiment heating of the first portion  
15 is performed in a first converter having a ceramic heating chamber and heating of the second portion is performed in a second converter having nickel materials in its heating chamber. Therefore, the respective first and second sample portions are oxidized in different chemical environments.  
20 The radiation generated by chemiluminescence of the sample in the ceramic converter is passed through a quartz filter and detected. The radiation generated by chemiluminescence of the sample in the nickel converter is passed through a red (infrared) filter and detected. The signal related to  
25 radiation passing through the quartz filter is subtracted from the signal related to the radiation passing through the red filter by a computer. The result is compared to certain predetermined threshold criteria to determine the presence or absence of certain nitrogen or hydrocarbon compounds of  
30 interest. Appropriate reject signals for a bottle sorting system are generated accordingly.

          Further scope of applicability of the present invention will become apparent from the detailed description given

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hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus, are not limiting of the present invention and wherein:

Fig. 1 is a schematic block diagram of the sampling and residue analyzing system disclosed in U.S. application Serial No. 07/890,863 illustrating a plurality of containers moving seriatim along a conveyor system through a test station, reject mechanism and washer station;

Fig. 2 is a block diagram also disclosed in U.S. application Serial No. 07/890,863 illustrating a possible implementation of the system of Fig. 1 in a detector system in which the contaminant being detected may be a nitrogen containing compound;

Fig. 3 is a schematic diagram of an improved analyzer system according to the present invention;

Fig. 4 illustrates graphs of signals detected and processed by the system of Fig. 3 for a sample having nitrogen containing compounds such as  $\text{NH}_3$ ;

Fig. 5 illustrates graphs of signals detected and processed by the system of Fig. 3 for a sample containing hydrocarbons such as diesel fuel or kerosene;

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Fig. 6 illustrates graphs of signals detected and processed by the system of Fig. 3 for samples containing an unknown contaminant affected in a similar manner by heating in two different converters; and

5 Fig. 7 illustrates graphs of signals detected and processed by the system of Fig. 3 for samples containing no contaminants of the type detectable by the present invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The disclosures of the aforementioned applications  
10 Serial Nos. 07/890,863 and 07/890,864 are incorporated herein by reference.

With reference to Fig. 1 of parent application Serial No. 07/890,863, there is illustrated a conveyor 10 moving in the direction of arrow A having a plurality of uncapped,  
15 open-topped spaced containers C (e.g., plastic beverage bottles of about 1500 c.c. volume) disposed thereon for movement seriatim through a test station 12, reject mechanism 28 and conveyor 32 to a washer system. To achieve higher test rates containers C could be touching each other rather  
20 than spaced. The contents of containers C would typically include air, volatiles of residues of contaminants, if any, and volatiles of any products such as beverages which had been in the containers. An air injector 14 which is a source of compressed air is provided with a nozzle 16 spaced  
25 from, but aligned with, a container C at test station 12. That is, nozzle 16 is disposed outside of the containers and makes no contact therewith. Nozzle 16 directs compressed air into containers C to displace at least a portion of the contents of the container to thereby emit a sample cloud 18  
30 to a region outside of the container being tested.

As an alternative to compressed air, CO<sub>2</sub> gas could be utilized as the injected fluid. Also, the compressed air or



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CO<sub>2</sub> gas could be heated to enhance volatility of the compounds being tested.

The column of air injected through nozzle 16 into a container C would be typically of the order of about 10 c.c. for bottle speeds of about 200 to 1000 bottles per minute. A rate of 400 bottles per minute is preferable and is compatible with current beverage bottle filling speeds. The desired test rate may vary with the size of the bottles being inspected and filled. Of course the bottles could be stationary or moving slower than 200 bottles per minute and the system would still work. Only about 10 c.c. of the container contents would be displaced to regions outside of the bottle to form sample cloud 18.

Also provided is an evacuator sampler 22 which may comprise a vacuum pump or the like coupled to a sampling tube or conduit 20. The tube is mounted near, and preferably downstream (e.g., about 1/16 inch) of the air injector 14 so as to be in fluid communication with sample cloud 18 adjacent to the opening at the top of containers C.

Neither nozzle 16 nor tube 20 contacts the containers C at test station 12; rather both are spaced at positions outside of the containers in close proximity to the openings thereof. This is advantageous in that no physical coupling is required to the containers C, or insertion of probes into the containers, which would impede their rapid movement along conveyor 10 and thus slow down the sampling rate. High speed sampling rates of from about 200 to 1000 bottles per minute are possible with the system and method of the present invention. The conveyor 10 is preferably driven continuously to achieve these rates without stopping or slowing the bottles down at the test station.

A bypass line 24 is provided in communication with the evacuator sampler 22 so that a predetermined portion

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(preferably about 90%) of the sample from cloud 18 entering tube 20 can be diverted through bypass line 24. The remaining sample portion passes to a residue analyzer 26, which determines whether specific substances are present, and then is exhausted. One purpose of diverting a large portion of the sample from cloud 18 is to reduce the amount of sample passing from evacuator sampler 22 to residue analyzer 26 in order to achieve high speed analysis. This is done in order to provide manageable levels of samples to be tested by the residue analyzer 26. Another purpose for diverting a portion of the sample is to be able to substantially remove all of sample cloud 18 by evacuator 22 from the test station area and divert the excess through bypass line 24. In a preferred embodiment the excess portion of the sample passing through bypass line 24 returned to air injector 14 for introduction into the subsequent containers moving along conveyor 10 through nozzle 16. However, it would also be possible to simply vent bypass line 24 to the atmosphere.

It should be understood that sample cloud 18 could be analyzed in situ without transporting it to a remote analyzer such as 26. It could also be transported to analyzer 26 by blowing rather than sucking.

A microprocessor controller 34 including an analog to digital converter is provided for controlling the operation of air injector 14, evacuator sampler 22, residue analyzer 26, a reject mechanism 28 and an optional fan 15. Container sensor 17 including juxtaposed radiation source and photodetector is disposed opposite a reflector (not shown) across conveyor 10. Sensor 17 tells controller 34 when a container arrives at the test station and briefly interrupts the beam of radiation reflected to the photodetector. Optional fan 15 is provided to generate an air blast towards sample cloud 18 and preferably in the direction of movement

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of containers C to assist in the removal of sample cloud 18 from the vicinity of test station 12 after each container C is sampled. This clears out the air from the region of the test station so that no lingering residues from an existing sample cloud 18 can contaminate the test station area when successive containers C reach the test station for sampling. Thus, sample carryover between containers is precluded. The duty cycle for operation of fan 15 is controlled by microprocessor 34 as indicated diagrammatically in Fig. 1. Preferably fan 15 is continuously operating for the entire time the rest of the system is operating.

A reject mechanism 28 receives a reject signal from microprocessor controller 34 when residue analyzer 26 determines that a particular container C is contaminated with a residue of various undesirable types. Reject mechanism 28 diverts contaminated rejected bottles, as to a conveyor 30, and allows passage of uncontaminated, acceptable bottles to a washer (not shown) on a conveyor 32.

An alternative option is to place the bottle test station downstream of the bottle washer in the direction of conveyor travel, or to place an additional test station and sample and residue analyzing system after the washer. In fact it may be preferable to position the test station and system after the washer when inspecting bottles for some contaminants. For example, if the contaminant is a hydrocarbon, such as gasoline which is insoluble in water, it is easier to detect residues of hydrocarbons after the bottles have been washed. This is because during the washing process in which the bottles are heated and washed with water, water soluble chemical volatiles are desorbed from the bottles by the heating thereof and then dissolved in the washing water. Certain hydrocarbons, on the other hand, not being water soluble, may then be sampled by a sampler 22

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downstream of the washer, to the exclusion of the dissolved, water-soluble chemicals. Therefore, the detection of such hydrocarbons can be performed without potential interference from other water soluble chemicals if the bottles pass  
5 through a washer before testing.

Referring to Fig. 2 there is illustrated a specific embodiment of a detector system for use with the sampling and analyzing system of Fig. 1 wherein like reference numerals refer to like parts. The detector system of Fig. 2 is also  
10 fully disclosed in parent application Serial No. 07/890,863 filed June 1, 1992. As illustrated, a nozzle 16 is provided for generating an air blast which passes into a container (not shown) being inspected. The air passing through nozzle 16 may be heated or unheated, it being advantageous to heat  
15 the air for some applications. Juxtaposed to the nozzle 16 is sample inlet tube 20 including a filter 40 at the output thereof for filtering out particles from the sample. Suction is provided to tube 20 from the suction side of pump 82 connected through a detector assembly 27.

20 A portion of the sample (for example, 90-95% of a total sample flow of about 6000 c.c. per minute), as described in connection with Fig. 1, is diverted through a bypass line 24 by means of connection to the suction side of a pump 46. Pump 46 recirculates the air through an accumulator 48, a  
25 normally open blast control valve 50, and back to the air blast output nozzle 16. A backpressure regulator 54 helps control pressure of the air blast through nozzle 16 and vents excess air to exhaust 57. Blast control valve 50 receives control signals through line 50A from microprocessor  
30 controller 34 to normally maintain the valve open to permit the flow of air to the nozzle.

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Electrical power is provided to pump 46 via line 46A coupled to the output of circuit breaker 76 which is in turn coupled to the output of AC filter 74 and AC power supply PS.

The detector assembly 27 in the embodiment of Fig. 2 is  
5 an analyzer which detects the residue of selected compounds such as nitrogen containing compounds in the containers being inspected by means of a method of chemiluminescence. This type of detector is generally known and includes a chamber for mixing ozone with nitric oxide, or with other compounds  
10 which react with ozone, in order to allow them to react, a radiation-transmissive element (with appropriate filter), and a radiation detector to detect chemiluminescence from the products of reaction. For example, when NO, produced from heating nitrogen compounds (such as ammonia) in the presence  
15 of an oxidant (e.g. oxygen in air), chemically reacts with the ozone, characteristic light emission is given off at predetermined wavelengths such as wavelengths in the range of about 0.6 to 2.8 microns. Selected portions of the emitted radiation of chemiluminescence, and its intensity, can be  
20 detected by a photomultiplier tube.

Accordingly, in the system of Fig. 2 ambient air is drawn in through intake 60 and air filter 62 to an ozone generator 64. Ozone is generated therein, as by electrical discharge into air, and is output through ozone filter 66 and  
25 flow control valve 68 to the detector assembly 27 wherein it is mixed with samples from containers input through intake tube 20, filter 40, flow restrictor 42, and converter 44. The sample from intake tube 20 is passed through a converter 44, such as an electrically-heated nickel tube, in which the  
30 temperature is raised to approximately 800°C to 1000° (e.g., about 900°C) before being input to detector assembly 27. Temperatures in the range of 400°C to 1400°C may also be acceptable. When nitrogen-containing compounds such as

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ammonia are so heated, NO (nitric oxide) is produced, and the nitric oxide is supplied to the chamber of the detector assembly 27. Compounds other than NO which may react with O<sub>3</sub> and chemiluminescence may also be produced in converter 44  
5 e.g., organic compounds derived from heating of gasoline, kerosene, or cleaning residue.

A temperature controller 70 supplied with electrical power through a transformer 72 is used to control the temperature of converter 44.

10 The samples in the detector assembly 27 after passage through its chamber are output through an accumulator 85 and pump 82 to an ozone scrubber 56, and to an exhaust output 57 in order to clear the residue detector for the next sample from the next container moving along the conveyor 10 of Fig.  
15 1. (As indicated above, an (optional) fan, not shown in Fig. 2, may be employed to help clear any remaining sample cloud from near the sample inlet tube 20.) Outputs from detector assembly 27 relating to the results of the tests are output through a preamp 84 to microprocessor 34 which feeds this  
20 information in an appropriate manner to a recorder 83. The recorder 83 is preferably a conventional strip recorder, or the like, which displays signal amplitude vs. time of the sample being analyzed.

The microprocessor 34 may be programmed to recognize, as  
25 a "hit" or the detection of a specific residue, a signal peak from a photodetector of the detector assembly 27 which is present in a predetermined time interval (based on the sensed arrival of a container at the test station) and whose slope and amplitude reach predetermined magnitudes and thereafter  
30 maintain such levels for a prescribed duration.

The microprocessor controller 34 also has an output to a bottle ejector 28 to reject contaminated bottles and separate them from bottles en route to a washer.

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A calibration terminal 86 is provided for residue analyzer 27 for adjusting the high voltage supply 26A associated with the detector assembly. Also provided is a recorder attenuator input terminal 88 connected to the  
5 microprocessor controller 34 for adjusting the operation of the recorder. Detector assembly 27 receives electrical power from the high voltage supply 26A.

Additional controls include operator panel 90 including a key pad and display section permitting an operator to  
10 control the operation of the detector assembly 27 in an appropriate fashion.

DC power is supplied to all appropriate components through DC power supply 78 coupled to the output of power supply PS.

15 An optional alarm enunciator 80A is provided for signaling an operator of the presence of a contaminated container. Alarm enunciator 80A is coupled to the output of microprocessor controller 34 via output control line 80C. A malfunction alarm 80B is also coupled to microprocessor  
20 controller 34 for receiving fault or malfunction signals such as from pressure switch 58 or vacuum switch 87 when pressures are outside of certain predetermined limits.

Other safety devices may be provided such as vacuum gauge 89, and back pressure control valve 54 for ensuring  
25 proper operation of the system.

Most components of the entire system of Fig. 2 are preferably enclosed in a rust-proof, stainless steel cabinet 92. The cabinet is cooled by a counter-flow heat exchanger 91 having hermetically separated sections 91A and 91B in  
30 which counter air flow is provided by appropriate fans.

The system illustrated in Figure 2 has a single detector assembly 27 for analyzing the sample evacuated into tube 20 and converter or converter 44. In most instances this system

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works quite well to detect either hydrocarbons or nitrogen containing compounds. However, sometimes a signal of interest may be hidden, or masked by background NOx (NO or NO<sub>2</sub>) signals. Also, background signals, particularly during  
5 periods of rapid variation in background, may result in an indication that a compound of interest is present even though the compound is absent - i.e., a "false positive". Background NOx could vary due to passage of a fork-lift truck in the plant in the vicinity of the testing apparatus; due to  
10 different atmospheres in which some of the bottles to be tested were stored; or due to traffic outside of the plant and other various causes.

In order to avoid false positives and to keep signals of interest from being hidden in background signals, a preferred  
15 embodiment of the present invention includes an improved sample analyzer system, portions of which are illustrated in Fig. 3. The system is similar in many respects to that of Fig. 2; however, converter 44, detector assembly 27, and preamp 84 of the Fig. 2 system are replaced by the components  
20 shown in Fig. 3.

With reference in detail to Fig. 3, a sample such as from sample cloud 18 emerging from a container to be inspected is evacuated into sample tube 20 and passes through filter 40 and flow restrictor 42. The sample is then split  
25 into two parallel flow lines connected to parallel converters P1, P2. Converter P1 is preferably a ceramic converter so that the portion of the sample being heated therein is heated in the presence of ceramic materials. Converter P2 is preferably a nickel converter (formed of or containing  
30 nickel) so that the portion of the sample being heated therein is heated in the presence of nickel oxide. The output of container P1 is connected to the input of a chemiluminescence detector assembly D1 and the output of the



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nickel converter P2 is connected to the input of a chemiluminescence detector assembly D2. Chemiluminescence detector assembly D1 is provided with a quartz output filter - e.g., a 0.19 micron cutoff filter - so that radiation of wavelengths greater than 0.19 microns emitted by chemiluminescence within detector assembly D1 passes through the quartz filter to a photomultiplier tube which converts the radiation signal into an electrical signal having a characteristic shape and amplitude for each substance to be detected at characteristic wavelengths for the respective substances. The radiation emitted is generated by the chemical reaction of the sample in the detector with ozone gas supplied thereto in a manner which is well known in the art. In other words, detector assembly D1 detects the presence of substances which emit characteristic wavelengths of radiation which will pass through a quartz filter.

Detector assembly D2, on the other hand, has an infrared output filter - e.g. a 0.6 micron cut-off filter - which will selectively pass radiation in the infrared (and longer wavelength) region of the spectrum corresponding to various nitrogen containing compounds.

In operation, a sample from cloud 18 is sucked through sample tube 20, filter 40, and flow restrictor 42 and is split into approximately equal portions to pass into and through the two converters P1, P2 arranged in parallel. Both converters P1 and P2 are heated to approximately 900°C. A temperature of 900°C is preferable, however, the system will achieve satisfactory results if the converters are heated to substantially the same temperature in the range of approximately 800°C. to 1400°C.

As stated above, converter P1 is a ceramic converter whose reaction chamber is lined with, a material such as aluminum oxide or the like. The other converter P2 is made

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of or contains nickel, e.g. converter P2 is a nickel alloy tube or a ceramic tube containing a nickel wire coil.

Typical dimensions for the converters P1 and P2 are approximately 15" long; 0.03-0.2" inside diameter; and  
5 typically 1/8" inside diameter, 1/4" outside diameter.

Detectors D1 and D2 are coupled to the outlets of the respective converters P1 and P2 and to a vacuum in order to draw the sample through the converters and the detectors. The outputs of the detectors D1 and D2 are connected through  
10 suitable amplifiers A1 and A2 to a microprocessor controller 34, which includes analog to digital converters and is operable to process the electrical signals S1 and S2 produced by the detectors D1 and D2 and provide outputs which include individual processed signals and a net signal which results  
15 from the subtraction of signals output from the respective detectors - e.g., a net signal (S2-S1).

Preferably, the flow resistance through converters P1 and P2, detectors D1 and D2, and flow lines associated with these components is designed to be relatively equal so that  
20 timewise variation of background is the same as measured by detectors D1 and D2. The main flow resistance (and hence flow rate) is set by the flow restrictor 42.

Figs. 4-6 show amplitude vs. time graphs of signals output from detectors D1 and D2 for various substances to be  
25 detected. Figs. 4-5 show signals with relatively high, time-varying backgrounds. Subtraction of signals produces a result (S2-S1) which is a positive(+) signal for detection of nitrogen compounds, and a negative(-) signal for detection of hydrocarbons, (olefins, are in diesel fuel or kerosene). The  
30 signal is positive for nitrogen containing compound detection (Fig. 4) because, at typical temperatures and flow rates employed, converter P1, which is ceramic, does not produce appreciable amounts of NO in the absence of nickel oxide.

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The signal ( $S_2 - S_1$ ) is negative for olefins (Fig. 5) because the signal  $S_1$  of detector D1 is larger than the signal  $S_2$  of detector D2 for at least two possible reasons. The first reason is that more signals related to olefin chemiluminescence are produced in the ceramic converter than in the nickel converter, and the second reason is that less of the chemiluminescence radiation produced in detector D1 is filtered out by the quartz filter of detector D1 than by the infrared filter of detector D2. In any event, a net negative signal ( $S_2 - S_1$ ) resulting from the subtraction is an indication of the presence of an olefin contaminant such as diesel fuel or kerosene.

Note that the signal ( $S_2 - S_1$ ) of Fig. 4 might be missed unless subtraction of signals is performed since the high level of background signals of  $S_2$  and  $S_1$  might permit the nitrogen compound signal to hide. Also, the importance of avoiding time shifts in flow through the converters P1, P2 and detectors D1, D2 is apparent, particularly for analysis under conditions where background levels vary rapidly and would not subtract to zero if time-shifting occurred.

The ceramic converter P1 apparently "cracks" the diesel fuel or kerosene to produce a double-bonded hydrocarbon, most probably an alkene such as 1-butene or propylene, which chemiluminesces with ozone ( $O_3$ ). Apparently in the nickel containing converter P2, some of the cracked material burns or reacts to form non-chemiluminescing compounds before as much of the alkene is formed in the nickel containing converter P2 as in the ceramic converter P1. This theory would seem to explain the result that for gasoline which already contains alkenes, the alkenes are apparently unaffected in passing through the converters. In fact, the converters are usually not necessary to detect gasoline by chemiluminescence.

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For gasoline contaminants the net signal ( $S_2 - S_1$ ) will typically be negative because the quartz filter of D1 attenuates less radiation than the infrared filter of D2.

In order to avoid missing other foreign substances such as chemicals from a cigarette in a container or sample being analyzed, the threshold levels of the individual signals  $S_1$  and  $S_2$  should be analyzed in addition to the net signal ( $S_2 - S_1$ ). See, for example, Fig. 6, in which it can be seen that for certain contaminants it's possible that subtraction of the signals  $S_2$  and  $S_1$  yields a net result of ( $S_2 - S_1$ ) nearly 0, even though each detector contains signal peaks which occur at a specified time (within a window relative to arrival of containers at the test station) and have a shape and amplitude which satisfy criteria for the presence of a contaminant. Thus if the peaks of the individual signals  $S_1$  and  $S_2$  are compared to threshold levels TL, the contaminant, such as cigarette residue, may be properly detected. The signals illustrated in Fig. 6 for  $S_1$  and  $S_2$ , respectively, indicate such peaks and therefore the system would indicate a hit and produce an appropriate reject signal. The sharp spike-like signals of Fig. 6 and those of Fig. 7 (which are for analysis of a sample illustrated to lack contaminants of the type and quantity to be detected), though above the threshold level (TL), lack the necessary shape characteristics to indicate the presence of a contaminant.

Accordingly, the microprocessor controller 34 in accordance with the appropriate software provided for the method of the present invention, not only subtracts signal  $S_1$  from  $S_2$  to determine the presence or absence of certain hydrocarbons or nitrogen containing compounds, but may also look at the individual signals  $S_1$  and  $S_2$  to determine how the individual signals compare to the predetermined threshold

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criteria. The possibilities of various detection logic criteria are indicated in the following table.

**Detection By Net Signal**

<u>S2-S1</u>	<u>Indicates Presence Of</u>	<u>Action</u>	<u>Drawing Figure</u>
+ (above + threshold)	Nitrogen (NH <sub>3</sub> )	Reject	Fig. 4
- (below - threshold)	Diesel Fuel, Kerosene	Reject	Fig. 5
0 (but S1 and S2 otherwise show peak of specified character)	Cigarette or other Contaminants	Reject	Fig. 6
0 (and S1 or S2 (or both) lack peak of specified character)	No Contaminant	Accept	Fig. 7

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

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What is claimed is:

1 1. A method of detecting selected compounds, including  
2 certain nitrogen containing compounds and/or hydrocarbons, in  
3 a sample by chemiluminescent gas phase reaction with ozone  
4 comprising the steps of:  
5       collecting the sample;  
6       dividing the sample into first and second portions;  
7       heating the first portion of the sample to a first  
8 predetermined temperature;  
9       heating the second portion of the sample to a second  
10 predetermined temperature;  
11       mixing the heated first portion of the sample with ozone  
12 to cause a chemical reaction therewith in order to generate  
13 radiation by chemiluminescence having characteristic  
14 wavelengths related to substances in said first portion;  
15       mixing the heated second portion of the sample with  
16 ozone to cause a chemical reaction therewith in order to  
17 generate radiation by chemiluminescence having characteristic  
18 wavelengths related to substances in said second portion;  
19       selectively detecting radiation emitted by  
20 chemiluminescence from the first portion of the sample;  
21       selectively detecting radiation emitted by  
22 chemiluminescence from the second portion of the sample;  
23       said heating and detecting steps being performed in a  
24 manner so as to yield a higher level of detected radiation  
25 from one of said portions of the sample than the other for at  
26 least some of the selected compounds;  
27       generating first electrical signals from the radiation  
28 selectively detected from the first portion of the sample and  
29 second electrical signals from the radiation selectively  
30 detected from the second portion of the sample; and

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31 comparing the first electrical signals with the second  
32 electrical signals in order to determine the presence or  
33 absence of selected compounds in the sample.

1 2. The method of claim 1 wherein said heating steps  
2 comprise passing the first portion of the sample through a  
3 converter having a heating chamber including ceramic  
4 materials and passing the second portion of the sample  
5 through a second converter having a heating chamber including  
6 nickel materials.

1 3. The method of claim 1 wherein said heating, mixing,  
2 detecting, and generating steps are performed at  
3 substantially the same times for said first portion as for  
4 said second portion and wherein the step of comparing  
5 includes the steps of subtracting the first electrical  
6 signals from the second electrical signals so as to cancel  
7 background signals in said portions and comparing the net  
8 result to first predetermined threshold criteria.

1 4. The method of claim 3 including the further steps of  
2 comparing each of the first and second electrical signals  
3 individually with second predetermined threshold criteria.

1 5. The method of claim 1 wherein said dividing step is  
2 performed in a manner to yield substantially equal portions  
3 of the sample.

1 6. The method of claim 1 wherein said heating steps are  
2 performed in first and second converters each heated to  
3 substantially the same temperature in the range of about 800°  
4 to 1000°C.

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1 7. A system for detecting selected compounds, including  
2 certain nitrogen containing compounds and/or hydrocarbons, in  
3 a sample by chemiluminescent gas phase reaction with ozone  
4 comprising:  
5 means for collecting the sample;  
6 means for dividing the sample into first and second  
7 portions;  
8 first converter means for heating the first portion of  
9 the sample to a first predetermined temperature;  
10 second converter means for heating the second portion of  
11 the sample to a second predetermined temperature;  
12 means for mixing the heated first portion of the sample  
13 with ozone to cause a chemical reaction therewith in order to  
14 generate radiation by chemiluminescence having characteristic  
15 wavelengths related to substances in said first portion;  
16 means for mixing the heated second portion of the sample  
17 with ozone to cause a chemical reaction therewith in order to  
18 generate radiation by chemiluminescence having characteristic  
19 wavelengths related to substances in said second portion;  
20 means for selectively detecting radiation emitted by  
21 chemiluminescence from the first portion of the sample;  
22 means for selectively detecting radiation emitted by  
23 chemiluminescence from the second portion of the sample;  
24 means for generating first electrical signals having  
25 amplitudes and durations related to the detected  
26 characteristic wavelengths of radiation emitted from the  
27 mixed first portion of the sample and second electrical  
28 signals having amplitudes and durations related to the  
29 detected characteristic wavelengths of radiation emitted from  
30 the mixed second portion of the sample; and  
31 means for comparing the first electrical signals with  
32 the second electrical signals in order to determine the  
33 presence or absence of selected compounds in the sample;



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34       said heating, mixing, detecting, and generating means  
35 being operable to process said first portion at substantially  
36 the same relative times as the processing of said second  
37 portion thereby to permit cancellation of background signals  
38 from said first and second electrical signals by said  
39 comparing means.

1   8.   The system of claim 7, wherein the first converter means  
2 has a heating chamber including ceramic materials and the  
3 second converter has a heating chamber including nickel  
4 materials.

1   9.   The system of claim 7 wherein the means for comparing is  
2 operable to subtract the first electrical signals from the  
3 second electrical signals and to compare the net result to  
4 predetermined threshold criteria.

1   10.  The system of claim 9 further including means for  
2 comparing each of the first and second electrical signals  
3 individually with predetermined threshold criteria.

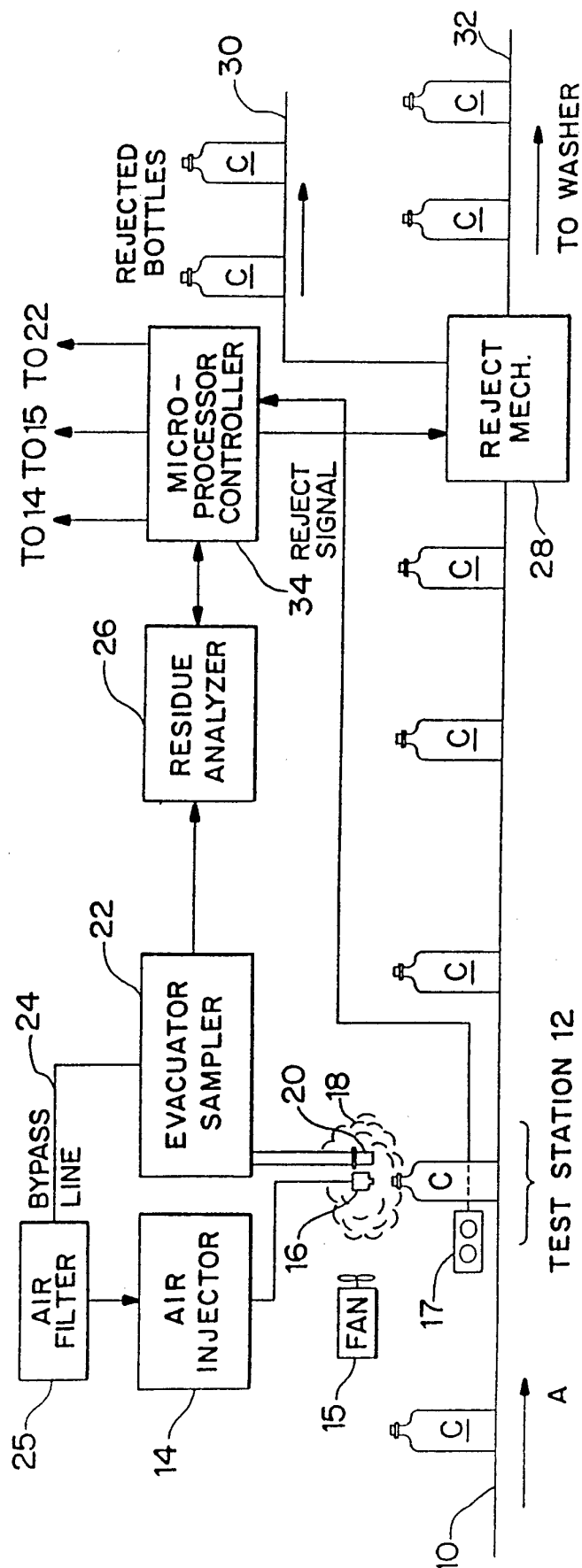
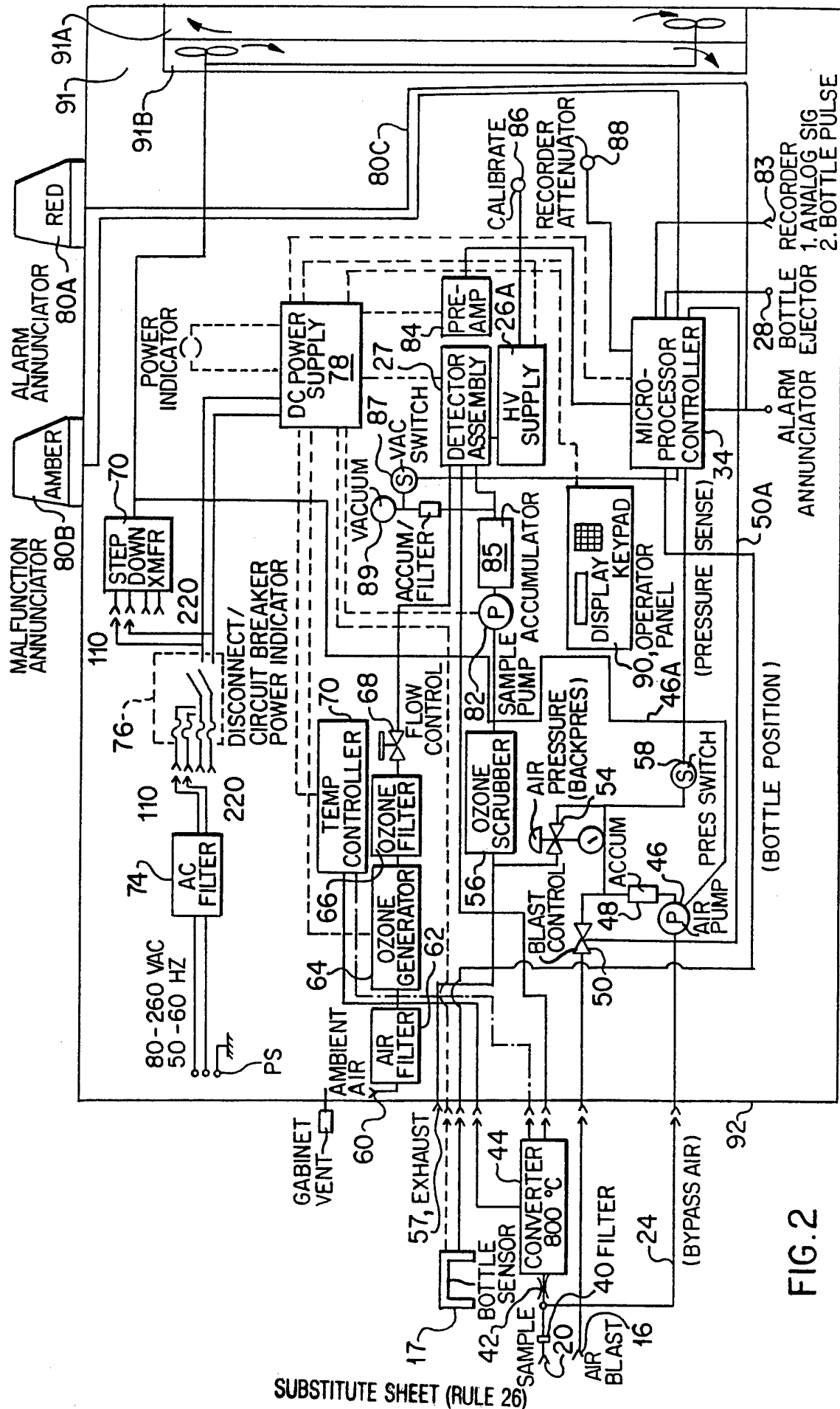


FIG. 1



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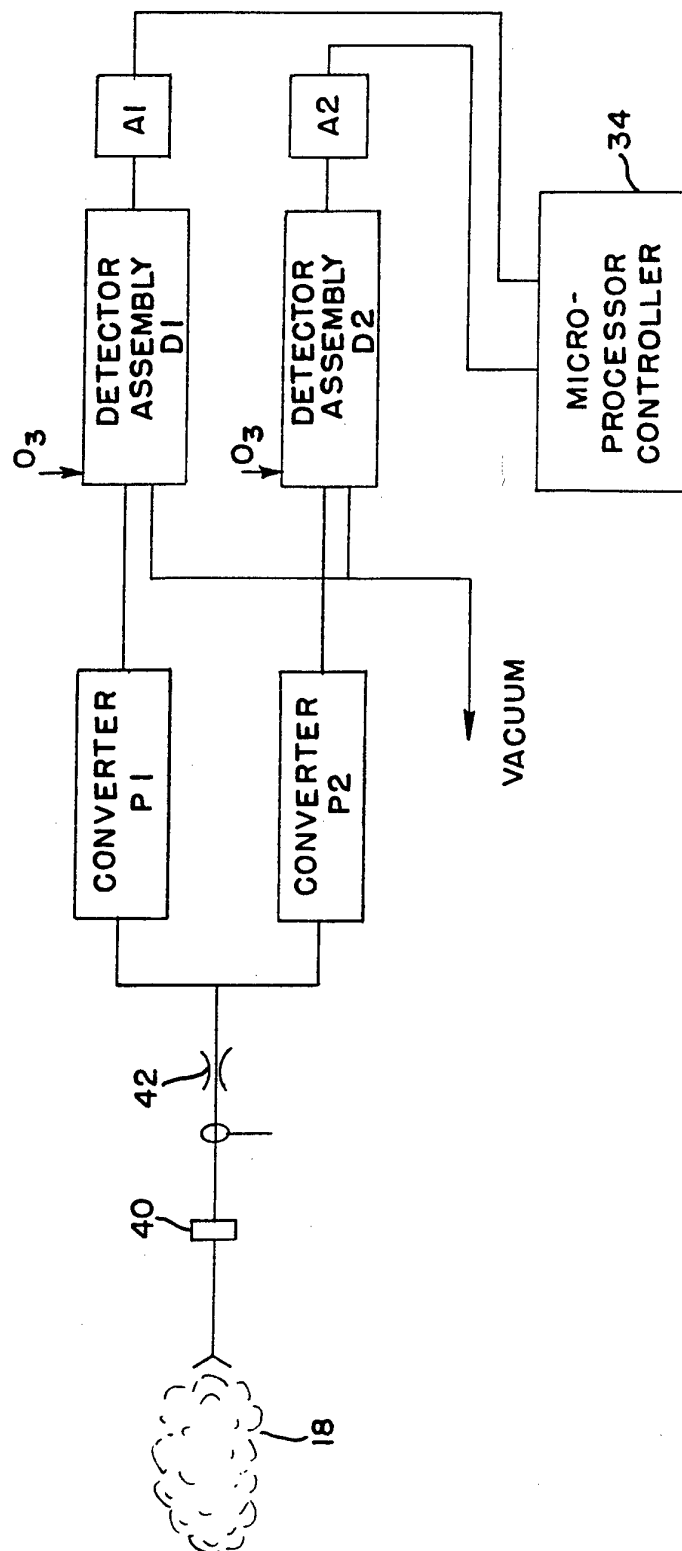


FIG. 3

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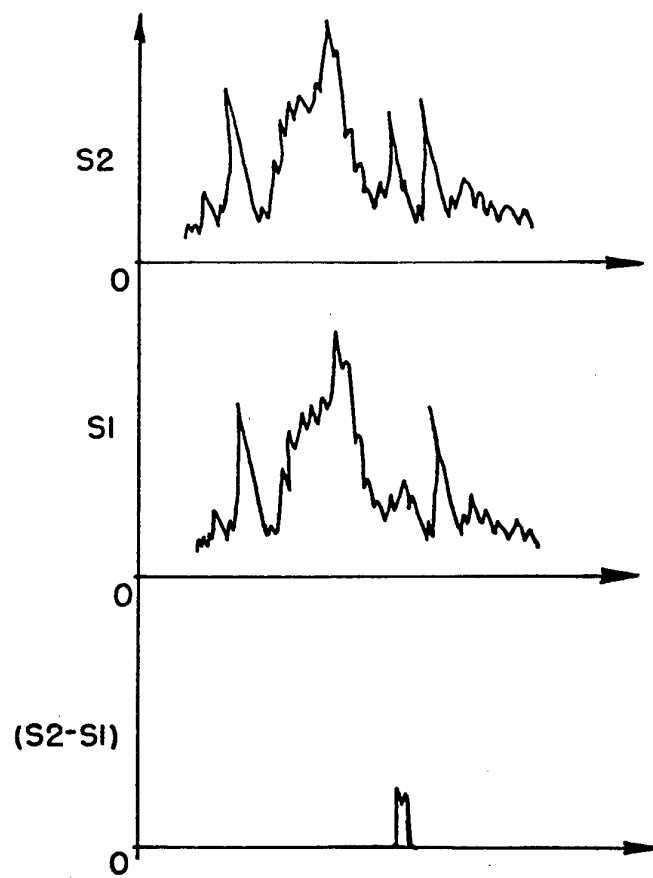


FIG. 4

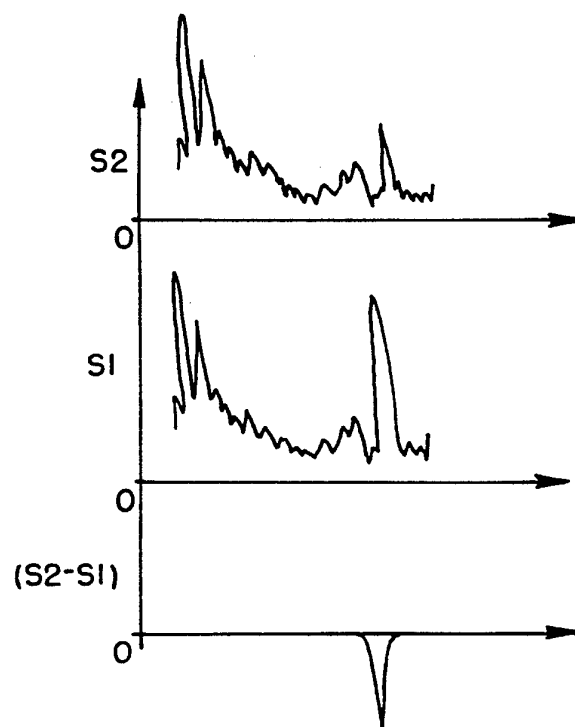


FIG. 5

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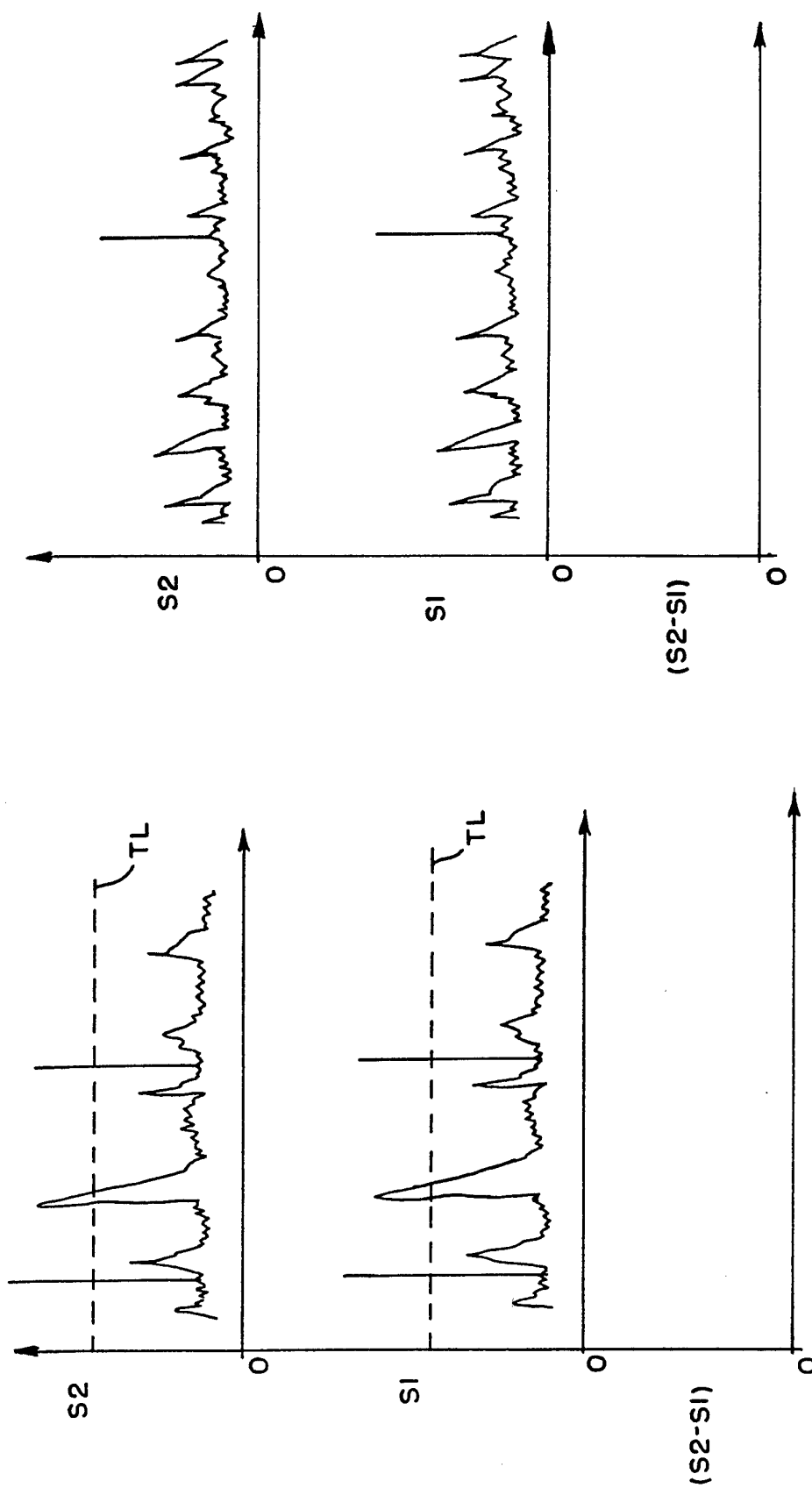


FIG. 7

FIG. 6

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/01590

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : G01N 21/76, 35/02; B07C 5/34

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/47, 43, 106, 172; 422/80, 82, 82.05, 82.08, 50, 93; 73/23.35; 209/3.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US,A, 5,255,072 (MIKASA ET AL) 19 October 1993, see column 6, lines 4-68 and claims 4 and 7.	1, 3-7 and 9-10
Y	US, A, 4,193,963 (BRUENING ET AL) 18 March 1980, see columns 6-10.	1, 3-7 and 9-10
Y	US, A, 4,775,633 (ROUNBEHLER) 04 October 1988, see column 4, lines 25-40 and column 6, lines 50-55.	2 and 8
Y	US, A, 3,870,468 (NETI) 11 March 1975, see column 3, lines 49-60.	2 and 8
A	US, A, 5,152,963 (WREYFORD) 06 October 1992.	1 and 7
A	US, A, 4,843,016 (FINE) 27 June 1989.	1 and 6-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be part of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z document member of the same patent family
*O document referring to an oral disclosure, use, exhibition or other means	
*P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 MAY 1994

Date of mailing of the international search report

MAY 25 1994

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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US94/01590

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A 5,096,834 (SAITO) 17 March 1992.	1 and 7



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/01590

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

436/47, 43, 106, 172; 422/80, 82, 82.05, 82.08, 50, 93; 73/23.35; 209/3.1