

[54] DETECTION DEVICE

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[51] Int. Cl. G01n 27/68

[58] Field of Search 23/232, 232 E, 254, 254 E, 23/230 PC; 73/23; 250/217

[56] References Cited

UNITED STATES PATENTS

3,528,779 9/1970 Fontijn 23/254 E X

3,540,851 11/1970 Vree et al. 23/232 E

OTHER PUBLICATIONS

Kiess et al., 7th Symposium (International) on Combustion, London & Oxford, 28 Aug.- 3 Sept. 1958, pp. 207- 209 relied on.

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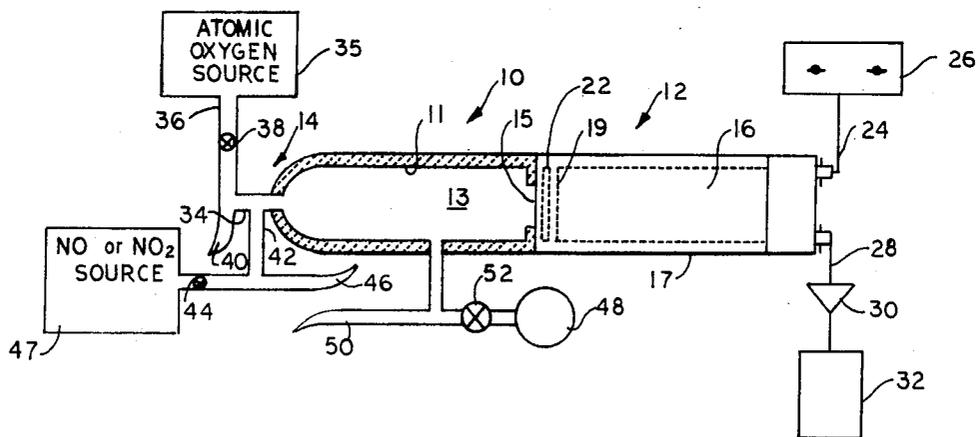
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[57] ABSTRACT

The presence of nitrogen containing compounds is detected by sampling vapor in the vicinity of the suspected compounds, reacting the vapor under conditions to convert the compound to nitric oxide. The nitric oxide is reacted with atomic oxygen with the chemiluminescent emission of light. This light is detected to determine the presence of the suspected compound.

13 Claims, 6 Drawing Figures



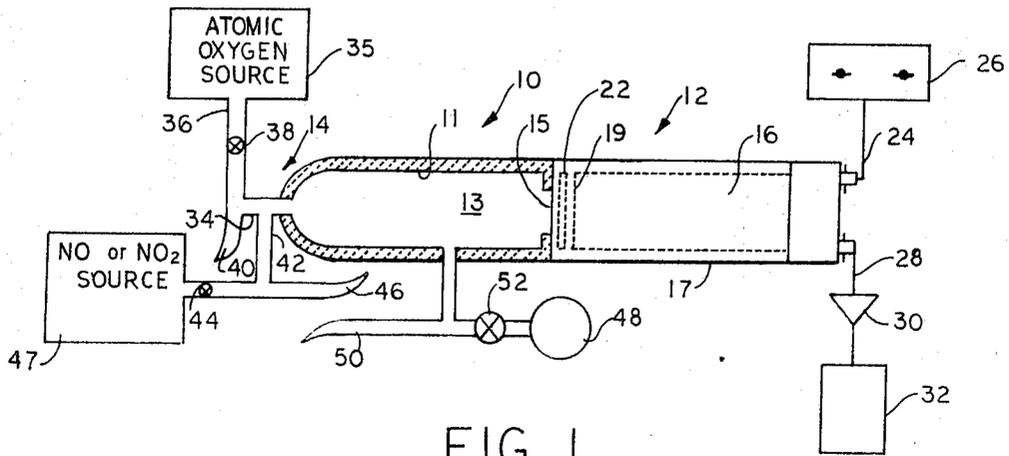


FIG. 1

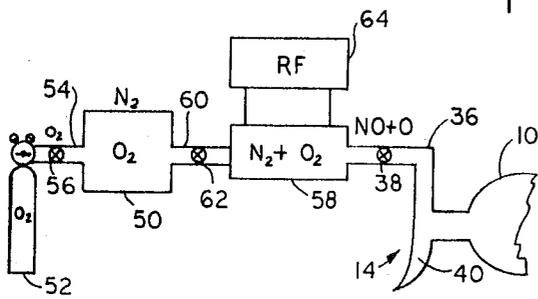


FIG. 2A

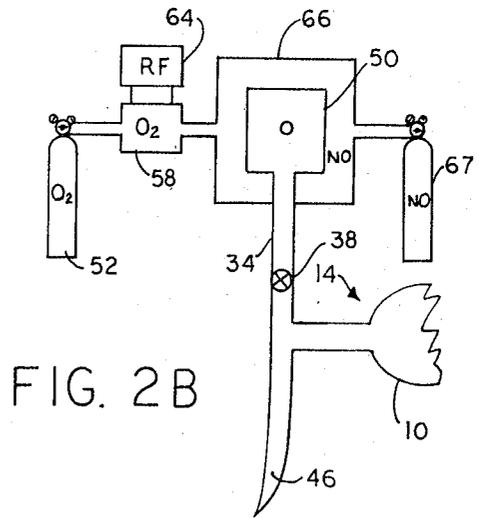


FIG. 2B

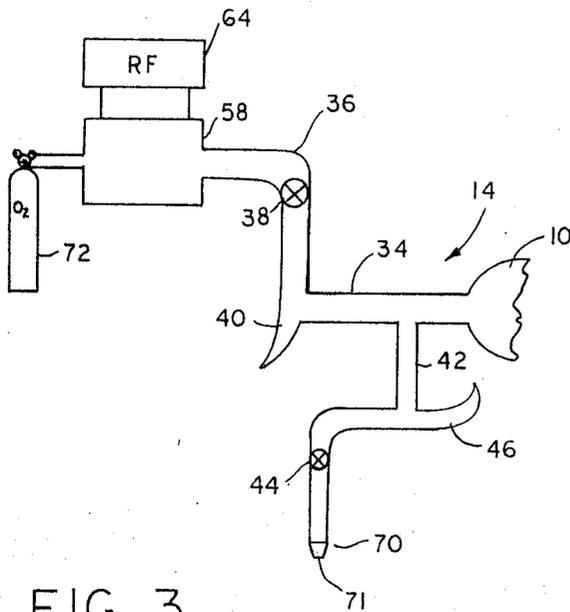


FIG. 3

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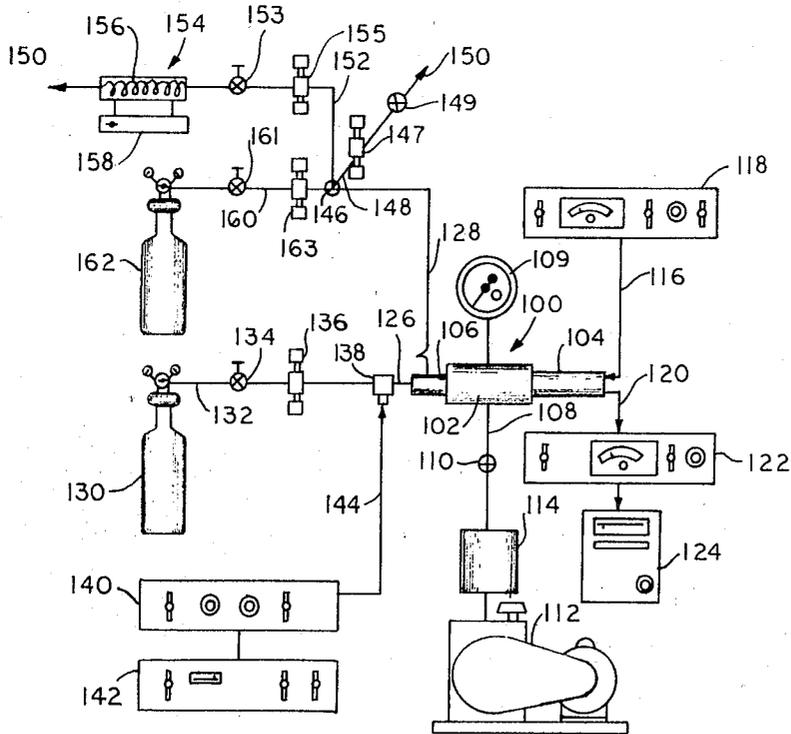
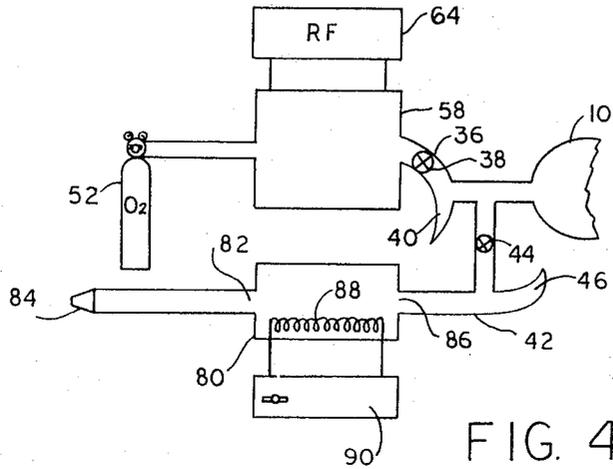


FIG. 5

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1

DETECTION DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the detection of nitrogen containing compounds and, more particularly, to the detection of these compounds by the chemiluminescent reaction of nitric oxide and atomic oxygen.

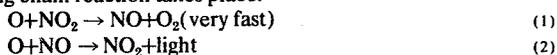
2. Description of the Prior Art

The analysis and detection of nitrogen containing compounds has so far relied on nonspecific physical methods such as mass spectrometry, or the formation of particulate matter. The results have not been completely satisfactory. Analytical techniques and apparatus are needed which are specific to nitrogen containing compounds.

SUMMARY OF THE INVENTION

The detection method in accordance with the invention relies on the chemiluminescent reaction of nitric oxide and atomic oxygen. This reaction yields light with a spectrum peaking in the violet. This light can be detected with high efficiency by a photomultiplier. The method of the invention may be utilized to determine the presence of nitrogen oxides in air, and also is useful in the detection of vapor of nitrogen containing compounds such as organic amines, nitroso, nitro, or nitrate compounds by thermally and/or catalytically converting the vapors to nitric oxide preliminary to the desired chemiluminescent reaction.

When gas containing nitric oxide (NO) or nitrogen dioxide (NO₂) is mixed with gas containing atomic oxygen, the following chain reaction takes place:



It is noted that the NO₂ which is a product of reaction 2 can again serve as reactant in reaction 1. Thus, a chain reaction occurs and more than one quantum of light can be produced per molecule of NO or NO₂.

The characteristics of available multipliers are such that 10^{5.7} photons/second can be detected easily. The forementioned chemiluminescent chain is capable of emitting 10^{20.1} photons/second for a liter of air containing one mole of nitric oxide (NO). Thus, the chemiluminescent method of the invention is capable of detecting 10⁻¹¹ parts of vapor in the atmosphere. This corresponds to a vapor pressure of approximately 10⁻⁸ mm. Hg., which is well below the vapor pressure of many nitrogen containing organic compounds.

The detector is, thus, capable of detecting trace amounts of nitrogen oxide vapors in an atmosphere or detecting the vapors being emitted from liquid or solid nitrogen containing organic compounds. The detection technique of the invention is also applicable to determining the integrity of containers by evacuating the container, filling the container with one of the reactants for the above chemiluminescent reaction and placing the container in an atmosphere of the other reactant. The contents of the container are then reacted under chemiluminescent conditions and the light emission detected by the invention to determine whether any gas has leaked into the container.

The apparatus of the invention is readily fabricated from available materials and can be compactly packaged into a portable instrument for use in airborne or land based craft. The instrument is very sensitive and reliable in the detection of compounds and the analysis of atmospheres for nitrogen oxide air pollutants. The apparatus may also be utilized as a security system to sense the suspicious entry or presence of people or animals or to detect leaks of organic nitrogen compounds from pipes or tanks.

These and other advantages of the invention will become readily apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

2

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view partly in section, of a detection system according to the invention;

FIG. 2a and 2b are schematic illustrations of leak detection systems in accordance with the invention;

FIG. 3 is a schematic view of an atmosphere sampling detector in accordance with the invention.

FIG. 4 is a schematic view of a system for detecting the presence of vapors of nitrogen containing compounds in accordance with the invention; and

FIG. 5 is a more detailed view of a system for the detection of the presence of nitrogen containing compounds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1 the nitric oxide detection system in accordance with the invention generally includes a reactor 10, a light detection assembly 12, and a gas inlet assembly 14. The reactor 10 may take many configurations. Preferably the reactor is a cylindrical tube which confines the gas flow along the axis of the photomultiplier tube 16. The interior surface 11 of the reactor 10 is preferably coated with a light-scattering substance such as magnesium oxide and the interior of the tube functions as a gaseous reaction chamber 13.

An aperture 15 is provided at one end of the reaction tube 10. The light detection assembly 12 comprises a photomultiplier tube housing 17 attached to the reactor opposite the aperture 15 for viewing the light emission from the reaction. The housing contains a photomultiplier tube 16 and a filter 22 disposed between the aperture 15 and the light sensitive face 19 of the photomultiplier tube 16. The high voltage lead 24 from the photomultiplier tube 16 is attached to a power supply 26. The signal lead 28 is attached to a microammeter 30. The output signal from the microammeter 30 is applied to a recording device such as a strip chart recorder 32.

The gas inlet assembly 14 includes an inlet branch 34. A first conduit 36 containing a valve 38 and a light baffle 40 communicates with inlet branch 34 and a source of atomic oxygen 35. A second conduit 42 containing a metering valve 44 and a light baffle 46, communicates with a source of gas 47 containing a suspected trace of nitric oxide or nitrogen dioxide and with the inlet branch 34. A vacuum pump 48 also communicates with the reactor 10 through a light baffle 50 and a throttling valve 52. The internal surfaces of the light baffles 40, 46 and 50 are blackened.

The apparatus is operated by reducing the pressure within reactor 10 to a level of about 1-10 mm. Hg., preferably 2-4 mm. Hg. Valves 38 and 44 are opened and the gas containing traces of nitrogen oxide and the supply of atomic oxygen enter chamber 10 and react with the emission of light. The vacuum pump 48 continually exhausts the reactor 10 and allows new samples to enter.

The energy of the chemiluminescent photons is distributed over the wavelength range of 4,000 to 8,000 Å. There are two strong oxygen transitions occurring during the reaction that emit light in the near-infrared that are not coupled with the NO chemiluminescent chain. These emissions can be eliminated by utilizing a broad band pass filter having a broad band transmission in the range of 4,200-6,000 Å, and a sharp cut off at each end of the range to exclude radiation not coupled with the chemiluminescent chain.

The light emitted by the reaction of atomic oxygen with nitric oxide is detected by a highly sensitive photomultiplier 16. These devices are commercially available with gains as high as 10⁸ having a photocathode with a radiant sensitivity at the wavelength of maximum response of about 15 milliamps per watt.

The detection system in accordance with the invention provides amplification both by the chemical amplification associated with the chain reaction and the photoelectric amplification associated with the photomultiplier. The chemical gain depends on the rate constants of the chemical chain

mechanism and the system parameters such as concentration of atomic oxygen in the detection chamber, volume of the detection chamber and light gathering efficiency of the detection chamber. The photoelectric gain depends on the quantum efficiency of the photoactive surface employed in the photomultiplier, the number of dynodes and their geometry, and on the system parameters such as overall voltage applied to the dynode chains and the energy of the chemiluminescent photons.

The detection system in accordance with the invention can detect trace amounts with commercially available photomultipliers. A typical photomultiplier has an overall sensitivity of about 5×10^4 amp/watt. High gain electrometers permit easy detection of 10^{-8} amp which corresponds to a detectability of 2×10^{-7} watts. This is equivalent to a flux of 5,000 A photons of 5×10^5 photons per second. The chemiluminescence of the nitric oxide reaction has a continuum between 4,000 and 8,000 A, peaking between 5,000 and 6,000 A. Since every molecule of nitric oxide can produce many quanta of light during the time typically spent in the reaction chamber, the chain reaction acts as a chemical amplifier. This is a consequence of the very fast rate of reaction.

The steady state rate of flux for the NO+O system is given by:

I (photons/sec) = $10^{28.4} [\text{NO}] [\text{O}] V$ In a one liter chamber having a light gathering efficiency, (ϕ) of 0.1 and an atomic oxygen concentration of 5×10^{-8} mole/liter at a pressure of 5 torr, the chemical amplification factor is:

$$I \frac{(\text{photons/sec})}{(\text{mole/liter})} = 10^{20.1} \phi$$

Thus, $10^{-14.4}$ moles of NO per liter of air at 5 mm. Hg in the detection chamber will produce an output current of 10^{-8} amp with the aforementioned photomultiplier. This corresponds to $10^{-12.2}$ moles of NO per liter of air at one atmosphere or one molecule of NO for every 10^{11} of air sampled, that is about 10^8 molecules NO/cc. air STP. This represents a practical detectability. Higher sensitivity can be realized by increasing light gathering efficiency and detecting output currents of 10^{-8} amp or lower which are all quite possible.

Under these operating conditions, the 1 liter reaction chamber should be swept out about every one quarter to one-fifth second. This corresponds to pumping speed of 4 to 5 liters per second at 5 mm. Hg. At this flushing rate, the concentration of oxygen atoms will have a steady state value only slightly over than the initial value.

Experiments indicate that the continuum emitted by the chemiluminescent chain increases proportionately with nitric oxide concentration, irrespective of the wavelength as long as the bands structure of the red region of the spectrum is filtered out. At a pressure of 2 to 3 mm. Hg., there is only a moderate quenching of the chemiluminescent emission between the exit and entrance to the reaction chamber. A chamber pressure of 5 mm. Hg. increases the recombination of atomic oxygen sufficiently to produce a noticeable reduction in emission. Increasing the volume of the chamber will increase the photomultiplier signal by increasing the photon flux impinging on the photomultiplier. However, a larger volume requires a corresponding larger pumping speed which increases the weight and power consumption of the vacuum system.

The sensitivity of the system was determined by observing photomultiplier signal as a function of the flows of 0.8 percent, 0.08 percent and 0.01 percent nitric oxide-nitrogen mixtures at constant oxygen flow. The oxygen supply was commercial high purity oxygen at 500 cc./min. Either resonance excitation, a far ultraviolet source (less than 1,850 A), or direct microwave excitation was used to dissociate the molecular oxygen. Detection at parts per million of nitric oxide was demonstrated. Sensitivity was dependent on the concentration of nitric oxide in the calibration mixture. Sensitivity also increased with increasing flow rate. Both of these effects are the consequence of the increase in the recombination rate of atomic oxygen via the chemiluminescent chain

and of the increase in total pressure with increasing flow. The effective concentration of atomic oxygen in the reaction chamber is decreased by increasing nitric oxide concentration and by increasing residence time in the chamber. Maximum gain of the chemical amplifier is realized for low concentrations of nitric oxide and fast flow rates, that is, very little reduction of the effective concentration of atomic oxygen in the reaction chamber.

The photomultiplier signal with zero added nitric oxide indicates chemiluminescent flux produced from traces of nitrogen in the oxygen supply. This signal decreases the overall gain of the system by saturating the photomultiplier which prevents utilization of the full gain of the photomultiplier. The catalytic recombination of oxygen atoms by nitric oxide between the point of generation and entrance into the reaction chamber reduces the effective concentration within the chamber. High velocity flows can lessen the effects of recombination as discussed above as does utilization of chamber pressures of about 2 to 3 torr. Increase in the photometric amplification and purification of the oxygen supply will allow at least another factor of 1,000 in the amplification and sensitivity of the system.

Very pure oxygen is commercially available in ultrahigh grade purities of 99.999 percent. This oxygen is produced by electrolytic dissociation of water and contains between 1-6p.p.m. of nitrogen. This is converted to nitric oxide by microwave discharge. The nitric oxide can be removed by selectively adsorbing the nitric oxide on silica gel, at low temperatures.

Another procedure for eliminating the traces of nitrogen is to prepurify the oxygen by one of the following methods:

1. Selectively absorbing the oxygen with heated barium oxide to form barium peroxide. The barium peroxide is cooled and evacuated to remove the residual gas. Heating the barium peroxide reverses the reaction producing chemically pure oxygen.
2. Pure oxygen can also be produced by the thermal decomposition of pure potassium permanganate at 240° C.
3. Reduction of nitrogen impurities in the electrolytically produced oxygen can be affected by degassing the water before electrolysis in a high vacuum system and storing and transferring the generated oxygen in the same system. Hydrogen impurities within the electrolytically produced oxygen can be removed by passing high-pressure oxygen through a heated bed of catalyst to convert the hydrogen to water. Water and hydrocarbon impurities can be removed through a series of liquid nitrogen traps containing adsorbents. This technique is a most reliable source of nitrogen-free oxygen.

Atomic oxygen is produced by the selective dissociation of oxygen. The dissociation can be effected by absorption of ultraviolet radiation in the 1,759-1,950 A region by a low-pressure oxygen flow which produces predissociation into ground state oxygen atoms. This radiation can be produced by microwave excitation of medium pressure resonance lamps containing krypton, xenon, mercury or bromine. The high temperatures of 1,900° C. attainable with a Nernst glow bar such as a zirconium oxide heater generate atomic oxygen thermally.

However, direct microwave excitation produces higher oxygen concentrations than either of the above techniques. Reduction of the power in the microwave cavity should reduce the rate of production of nitric oxide without reducing the oxygen atom generation rate an equivalent amount. When the current in the oscillator stage of the microwave generator was varied, the background signal could be reduced without appreciably affecting the sensitivity of the detection system to nitric oxide.

In FIGS. 2a and 2b the source of nitric oxide and monatomic oxygen is utilized as a leak detector for a container 50. In FIG. 2a the evacuated container 50 is fed a metered supply of chemically pure oxygen from tank 52 through a line 54 containing a metering valve 56. The output from con-

tainer 50 is fed to a microwave cavity 58 through a line 60 containing a valve 62. The microwave cavity 58 is subjected to a radiofrequency discharge from discharge source 64. If container 50 contains any leaks, nitrogen from the air will enter the container 50 and contaminate the pure oxygen with nitrogen. When this mixed gas is passed through the radio frequency discharge, atomic oxygen and nitric oxide will be produced. This chemiluminescent gas will pass through a line 36 containing a valve 38 the light baffle 40 into reactor 10 where the resulting light will be detected by photomultiplier 16.

In the embodiment illustrated in FIG. 2b chemically pure oxygen flows from source 52 into the microwave cavity 58 before entering container 50. The container is disposed within a larger enclosure 66. Enclosure 66 is pressurized with nitric oxide from cylinder 67. If there are any leaks present in container 50, the atomic oxygen produced by the radiofrequency discharge from source 64 will be contaminated with nitric oxide. When these gasses are fed to the inlet assembly 14 to the reactor 10, the chemiluminescent emission will be detected by photomultiplier tube 16.

The oxygen supply illustrated in FIG. 3 can be utilized for direct determination of nitrogen dioxide vapors in air. The gas inlet assembly 14 in this case includes, a sampling nozzle 70 containing a pinhole aperture 71 for collecting the surrounding air. The air is delivered to the inlet branch 34 through conduit 42 containing a metering valve 44, a light baffle 46. Atomic oxygen enters the branch 34 through the conduit 36. Suitably, atomic oxygen is generated from an ultrapure supply container 72. The oxygen supply passes through a microwave cavity 58 and is subjected to an RF discharge from source 64. The two streams combine within the inlet branch 34 and react axially within reactor chamber 13, to form nitric oxide with chemiluminescent emission of characteristic light. The light emission is detected by photomultiplier tube 16.

Carbon dioxide or carbon monoxide or sulfur dioxide or sulfur monoxide impurities in the atmospheric air do not lead to chemical amplification. The reactions of carbon dioxide and sulfur dioxide are endothermic while that of nitrogen dioxide is exothermic. The slower rate of their oxidative combination reactions will not support chain reactions.

The gas inlet assembly illustrated in FIG. 4 is intended for use in the collection of vapors of nitrogen containing compounds. The vapor collection system of FIG. 4 includes a conversion unit 80 designed to convert organic nitrites, nitrates, or amines to nitric oxide. The unit 80 can affect decomposition by thermal and/or catalytic means. The unit 80 has an inlet port 82 communicating with a sampling nozzle 84, and an output port 86 communicating with conduit 42. The interior of unit 80 may be provided with a heating wire 88 which is connected to a power supply 90. The interior surfaces of the unit 80 or the surface of wire may be coated with a catalyst such as a metal, suitably nickel, platinum, copper or their alloys which participate in the conversion and decomposition of the nitrogen containing vapor compounds.

An oven temperature of 1,250° K. will decompose organic nitrites and nitrates within microseconds. Under these same conditions, an organic nitro compound will pyrolyze at a much slower rate but it still will take no more than 3 milliseconds to decompose 90 percent of the molecules. Therefore, pyrolysis of these compounds can be regarded to take place instantaneously since the residence time of a gas flowing with a convenient flow rate can be several orders of magnitude larger than the lifetime of the molecules. Traces of organic amine vapors in air when heated in a conversion unit to about 1,800° F. in the presence of a noble metal catalyst such as platinum will be converted to nitric oxide. The output from the unit 80 is combined with a source of atomic oxygen within reactor 10. A chemiluminescent reaction proceeds which is detected by photomultiplier tube 16. The detection of animal vapors forms the basis of a detection unit for people or animals. The output from the ammeter may be connected to an alarm system or transmitted silently to remote stations to indicate presence of people or animals in the vicinity of the detector.

Nitrobenzene was introduced into pyrolysis unit 80 by passing purified air over a liquid sample of nitrobenzene at room temperature. A quartz tube having a 25 mm. I.D., 33 cm. long and operated at a pressure of 1,020 mm. Hg produced 2 percent conversion at 1,000° K. When this unit was packed with copper gauze having a surface coating of oxide, conversion efficiency increased by a factor of 10. A third pyrolysis unit constructed of copper tubing having an I.D. of 1.5 mm. and fashioned into a tight coil had a conversion efficiency of 70 percent which became essentially independent of airflow above 15 ml./min. 100 percent conversion was obtained in a further pyrolysis unit comprising a small quartz tube containing an internal nichrome heater operated at red heat. The nichrome wire operated both as a catalyst and a source of thermal energy. The metal catalyst not only increases the combustion efficiency, but also reduces the pyrolysis temperature.

A problem which must be accommodated is that of background which might interfere with detection. There are two kinds of background: (1) oxides of nitrogen and (2) naturally or normally occurring organic nitroso, nitro, amine or nitrate compounds, which will necessarily give a false positive signal. The first type of signal may come from auto exhaust, though, there is no known wide spread source of false signals of the second type.

Referring now to FIG. 5, more detailed detection system is disclosed which includes provision for analysis of background and calibration of the system. The system includes a reactor 100 which includes a central cylindrical reaction chamber 102 joined at one end by a photomultiplier housing 104 and at the other end by an inlet chamber 106. A vacuum conduit 108 and pressure gauge 109 also communicate with chamber 102. The conduit 108 contains a throttling valve 110 and communicates with a mechanical vacuum pump 112 through a copper gauze reactor 114. The reactor 114 converts the residual oxygen and oxides to harmless products before entering the vacuum pump 112.

A high voltage lead 116 connects the photomultiplier tube to a photomultiplier power supply unit 118 and a signal lead 120 connects the photomultiplier tube to a picoammeter 122. The output from the ammeter 122 is applied to a strip chart recorder 124.

The inlet chamber 106 receives a supply of atomic oxygen through conduit 126 and a supply of nitric oxide vapor through conduit 128. The supply of atomic oxygen emanates from a regulated oxygen storage cylinder 130. The oxygen flows from cylinder 130 through a line 132 containing a toggle shutoff valve 134 and a double-patterned, metering vernier valve 136, and an RF inductor or microwave cavity 138. The microwave cavity is powered by an RF oscillator 140 and RF power supply 142 through a lead 144.

The nitric oxide supply conduit 128 is fed from three alternate sources through a 3-way rotary valve 146. One source comprises a conduit 148 terminating in a nozzle 150 which contains a shutoff valve 149 and a metering valve 147. The second source comprises a conduit 152 containing in sequence a sampling nozzle 150, a pyrolysis unit 154, a toggle shutoff valve 153 and a double-patterned, vernier metering valve 155. The pyrolysis unit 154 contains a heating coil 156 powered by a power supply 158.

The third source of nitric oxide is a calibration source comprising a conduit 160 containing in sequence a regulated gas cylinder 162 containing nitric oxide and carrier gas, a toggle shutoff valve 161 and a double-patterned vernier metering valve 163.

To conduct an analysis in accordance with the invention, the vacuum pump 112 is turned on to reduce the pressure in the reactor 100 to about 3 mm. of Hg. The system is first calibrated by turning rotary valve 146 toward conduit 160 and opening valves 161 and setting valve 163 while closing valves 153 and 149. Valve 134 is opened and valve 136 regulated to a desired flow rate. RF oscillator 140 and power supply 142 are turned on to create a supply of atomic oxygen. The chemiluminescent reaction output is utilized to calibrate am-

meter 122 and recorder 124. Valve 161 is then closed, an the rotary valve 146 turn toward conduit 148 regulated by means of the metering valve 147. The photomultiplier output is again recorded to determine the presence of nitrogen dioxide (NO₂) to provide a background signal. This signal may be utilized to reset the zero level of the recorder 124 and ammeter 122.

Valve 149 is again closed and the rotary valve 146 turn toward conduit 152. Shutoff valve 153 is opened and metering valve 155 set to the desired level. The heater power supply 158 is adjusted to provide a temperature within the pyrolysis unit 154 of, at least about 1,250° K. The pyrolysis unit 154 converts the mixture of vapor of organic nitrogen compounds, and air to nitric oxide which combines with the atomic oxygen within reactor 100 with the chemiluminescent emission of light. The characteristic light output is detected and measured by the photomultiplier tube and is recorded by the recorder 124.

The type of nitrogen-containing compounds being pyrolyzed in the furnace can be distinguished by varying the furnace temperature and using various catalysts. If the temperature is lowered to 700° K, the organic nitrites and nitrates should take about 10⁻² sec to decompose, while the organic nitro compounds will pass through the furnace unchanged. Thus, the signal of a pyrolysis temperature of 1,250° K represents the total nitrogen-containing organic compounds, while the smaller signal at an oven temperature of 700° K gives an estimate of the amount of organic nitro compounds present.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, alterations and modifications are all permissible without departing from the spirit and scope of the invention as defined in the following claims.

We claim:

1. A method of detecting the presence of nitrogen containing compounds selected from the group consisting of nitroso, nitro, nitric and amino compounds comprising the steps of:
 - sampling the atmosphere in the vicinity suspected of containing said compounds to obtain a vapor sample;
 - heating said sample to thermally convert the compound into an oxide of nitrogen;
 - adding a supply of atomic oxygen to the converted vapor to form a mixture;
 - reacting said mixture in a chemiluminescent reaction yielding nitric oxide with light emission characteristic thereof; and measuring said emitted light.
2. A method according to claim 1 in which said compounds are heated to a temperature of at least about 1,800° F and said heating is conducted in the presence of oxygen and in the presence of a metal catalyst.
3. A process according to claim 1 in which said supply of atomic oxygen is formed by subjecting a very pure stream of

oxygen to a radiofrequency discharge.

4. A process according to claim 1 in which the chemiluminescent reaction is conducted at a reduced pressure.

5. A method according to claim 1 in which said mixture is removed from a closed container containing a first member selected from said vapor sample or said supply and said container is surrounded by a higher pressure atmosphere of said other member.

6. A method according to claim 5 in which said first member is oxygen, said atmosphere comprises nitrogen and the output from said chamber is subjected to a radiofrequency discharge to form a mixture of nitrogen oxide and atomic oxygen.

7. An apparatus for detecting the presence of nitrogen containing compounds comprising in combination:

- means for sampling the atmosphere in the vicinity suspected of containing a nitrogen containing compound;
- thermolytic reactor means receiving said sample for converting said nitrogen compound into an oxide of nitrogen;
- source means containing a supply of atomic oxygen;
- reactor means receiving said converted sample and said supply for chemiluminescent reaction thereof to form nitric oxide and characteristic emission of light; and
- photodetector means coupled to said reactor for detection of said characteristic emission.

8. An apparatus according to claim 7 in which said thermolytic reactor means includes a reactor chamber, means for heating the chamber and a nitrogen oxide conversion catalyst disposed within the chamber.

9. An apparatus according to claim 7 in which said source means comprises a supply of diatomic oxygen, a chamber for receiving said supply and a radiofrequency source coupled to said chamber for subjecting said diatomic oxygen to a radiofrequency discharge for conversion thereof to atomic oxygen.

10. An apparatus according to claim 7 further including closed container means for receiving a first gas selected from said sample or said source and means for applying said other gas to the exterior of said container whereby said chemiluminescent reactable mixture is formed only when said container contains a leak and chemiluminescent emission in said reactor detects said leak.

11. An apparatus according to claim 7 in which said reactor is a cylindrical tube having an internal light reflective surface, said reactor containing axial inlet means for receiving said sample and supply and an opposed axial light output aperture.

12. An apparatus according to claim 11 further including vacuum pump means coupled to said tube.

13. An apparatus according to claim 12 further including light baffle means disposed in said inlet means and in the line coupling said vacuum pump to said tube.

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