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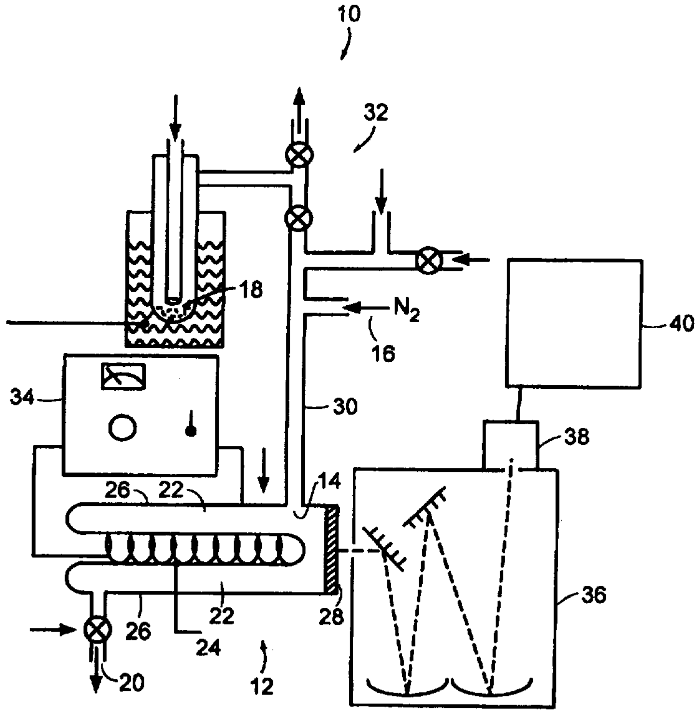
(57) Abstract

An active nitrogen energy transfer (ANET) system utilizing excitation to the Herman infrared spectrum and direct detection for rapid and sensitive analysis of materials for the presence of hydrocarbons, both chlorinated and non, heavy metals and transuranic compounds is disclosed. Samples to be analyzed are introduced into active nitrogen where only a few characteristic emissions are emitted. The ANET system is suitable for miniaturization because it is highly efficient, it can operate at atmospheric pressure, and it produces emission spectra that is simple to analyze. This ANET system has relatively high sensitivity to heavy metals compared with atomic absorption systems.



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Atomic and Molecular Species Analysis By Active Nitrogen Energy Transfer

Field of the Invention

The invention relates generally to the field of analyzing atomic and molecular species by observing their emissions spectra for characteristic emissions. In particular, the invention relates to methods and apparatus for analyzing atomic and molecular species that are excited by contact with excited metastable nitrogen molecules by observing their emissions spectra for characteristic emissions.

Background of the Invention

Emission spectroscopy is a well known analytical technique in which atomic and molecular species, in the vapor phase, are excited to emit a spectrum of fluorescent radiation. The emission spectrum and intensity of the fluorescent radiation are analyzed to determine which species are present and the concentration of each species. Various methods have been used to excite atomic species to energy levels where fluorescent radiation is emitted. These methods include the use of arcs, sparks, flames, and metastable excitation. Metastable excitation involves contacting the species with metastable atoms of an excited gas in a flowing gaseous medium. Metastable excitation is advantageous because it is more efficient and it allows for detection of trace metals with high sensitivity.

U.S. Patent 4,150,951, Capelle et al., discloses methods and apparatus for detecting and quantitatively measuring trace amounts of metals and other fluorescing species in the gas phase by introducing a species to be analyzed into a gas stream containing an energetic metastable species of nitrogen or a noble gas. The species to be analyzed are excited to higher energy levels by contact with the metastable exciting species, and subsequently emit fluorescence at characteristic wavelengths. The methods disclosed produce metastable species by subjecting a gas stream containing nitrogen, or a noble gas, to a microwave discharge at pressures of less than 10 Torr.

U.S. patent 4,148,612, Taylor et al., also discloses methods and apparatus for detecting and quantitatively measuring trace metals and other fluorescing species in the gas phase by introducing a species to be analyzed into a gas stream containing an energetic metastable species of nitrogen or a noble gas. Several methods of producing metastable atoms or molecules are disclosed, including methods utilizing microwave discharges and cold-cathode discharges. No dielectric barrier is utilized between the cathode and the anode in the cold-cathode discharge methods. The apparatus and methods are specifically directed to measuring trace impurities such as water, carbon dioxide, carbon monoxide, and methane which may exist in helium-based cooling systems.

U.S. patent 4,309,187, Dodge et al., discloses methods and apparatus which utilize a dielectric barrier discharge for detecting and quantitatively measuring trace metals and other fluorescing species in the gas phase. A metastable energy level of nitrogen is created by flowing nitrogen containing gas through a dielectric field generated by a dielectric barrier discharge at pressures from 1-300 Torr. Typically, the pressure is 10 Torr or below. The use of a dielectric field, at these pressures, enables the formation of the $A^3\Sigma_u^+$ nitrogen energy state with no population of the higher vibration levels of the $B^3\Pi_g$ state. Therefore, the metastable species generated demonstrate Begard-Vaplan emission with energy levels of 6.1-9.7 eV. The emission is observed in the afterglow region.

Prior art methods and apparatus for analyzing species in the gas phase that utilize metastable excitation have numerous limitations. Prior art methods and apparatus do not use coincident excitation, transfer, and detection and, thus, have limited sensitivity. Their sensitivity is limited because detection of the species occurs downstream from the excitation and transfer of energy from the metastable exciting species to the species to be analyzed. Substantial sensitivity loss occurs because of quenching and radiative loss that occurs in transit from the excitation/transfer region to the detection region.

In addition, prior art methods and apparatus are of limited practical use because they do not correct the detected signal for changing concentrations of exciting nitrogen metastables. Moreover, prior art apparatus are not suitable for miniaturization because they operate at pressures less then atmospheric pressure and, therefore, require the use of a vacuum pump. Also, the prior art excitation apparatus and methods excite the species to relatively high energy levels and, thus, produce complex spectra which require sophisticated analysis.

It is therefore a principal object of this invention to provide high sensitivity methods and apparatus for analyzing species in the gas phase that utilize metastable excitation and provide coincident excitation, transfer, and detection. It is another object of this invention to compensate for changing concentrations of exciting nitrogen metastables in such methods and apparatus. It is another object of this invention to provide an apparatus for analyzing both atomic and molecular species that is suitable for miniaturization because it utilizes a dielectric barrier discharge which operates at atmospheric pressure and because it produces a relatively simple spectra which is easy to analyze.

Summary of the Invention

A principal discovery of the present invention is that the intensity of Herman infrared radiation (HIR) is linearly related to the concentration of nitrogen metastables. Moreover, the intensity of the HIR increases with pressure from vacuum to atmospheric pressure. Another principle discovery is that analyte concentrations may be accurately determined under a variety of sampling conditions by correcting the analyte intensities for varying nitrogen metastable concentrations employing the Herman infrared band.

Another principal discovery is that active nitrogen energy transfer (ANET) utilizing the Herman infrared band may be used for high sensitivity analysis of both atomic and molecular species of metals, non-metals, and compounds. High sensitivity analysis has been demonstrated for copper, lead, aluminum, silver, nickel, mercury, mercuric chloride, chlorocarbons, hydrocarbons, cadmium, arsenic, selenium, and chromium. ANET utilizing the Herman infrared band may be used for high sensitivity analysis of numerous other elements including bismuth, bromine, chlorine, germanium, iodine, sulfur, antimony, tin, tellurium, europium, hafnium, magnesium, silicon, thallium, yttrium, zinc, gold, boron, barium, beryllium, calcium, cobalt, cesium, iron, gallium, indium, iridium, lithium, molybdenum, sodium, niobium, phosphorus, palladium, platinum, rhenium, rhodium, strontium, tantalum, thorium, titanium, vanadium, tungsten, zirconium, potassium, manganese. ANET utilizing the Herman infrared band may also be used for high sensitivity analysis of radioactive elements such as uranium and technetium.

ANET utilizing the Herman infrared band is useful for detecting atomic and molecular species in a variety of applications including process stream monitoring, stack gas monitoring and emissions control, and hazardous waste detection. For example, ANET utilizing the Herman infrared band may be used to monitor, with a single measurement, the major categories of hazardous waste, including transuranic compounds, hydrocarbons, chlorocarbons, and heavy metals. ANET may also be used for detecting dissolved metals in oil, including elemental mercury and mercuric chloride, lead, copper, aluminum, silver, and nickel. It has been discovered that ANET utilizing the Herman infrared band is a more sensitive technique for measuring heavy metals than prior art atomic absorption spectrometry techniques.

It is another principal discovery that relatively high sensitivity can be achieved with coincident excitation, transfer, and detection. Direct detection at the location where transfer of energy from the metastable exciting species to the species to be analyzed occurs, allows for detection of emitted radiation having very low signal-to-noise ratios which may be undetectable downstream due to quenching and radiative loss that occurs in transit from the excitation/transfer region to the detection region.

It is another principal discovery that an ANET system for analyzing both atomic and molecular species with high sensitivity may be configured for miniaturization. It has been determined that ANET systems utilizing a dielectric barrier discharge and operating at atmospheric pressure may be configured to be very compact. Such ANET systems may operate with relatively low power and high efficiency and produce a relatively simple spectra which is easy to analyze.

Accordingly, the present invention features a method for analyzing atomic and molecular species. A dielectric-barrier discharge vessel having a discharge region defined by first and second electrodes is provided. At least one of the first or second electrodes is surrounded by a dielectric material. A partial pressure is established by introducing species to be analyzed and molecular nitrogen into the dielectric-barrier discharge vessel. The partial pressure may be approximately between 1 Torr and atmospheric pressure.

An alternating potential is applied across the electrodes. The amplitude of the potential may be approximately 1-50 kV and the frequency may be approximately 15Hz-3kHz. The alternating potential forms a discharge that produces active nitrogen. The energy of the active nitrogen may be substantially in the Herman infrared spectrum. The mean temperature of electrons in the discharge is approximately between 2-10 eV. The active nitrogen excites atoms and molecules of the species to be analyzed in the discharge region.

Characteristic emissions of the metal, non-metal, and compound species to be analyzed are directly detected from the discharge region of the discharge vessel. The species can be simultaneously detected. Detection may be accomplished with one or more optical filters optically coupled to one or more photomultiplier tubes. In another embodiment, detection may be accomplished with a scanning monochromator and a detector.

In another embodiment, the present invention features an apparatus for analysis of atomic and molecular species. The apparatus includes a dielectric-barrier discharge vessel for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to the atomic and molecular species. The discharge vessel may be formed of quartz, glass, or ceramic tube. Borosilicate glass may also be used.

In addition, the discharge vessel includes an inlet for introducing molecular nitrogen and a sample to be analyzed. Within the discharge vessel, a discharge region is defined by a first electrode surrounded by a dielectric and a second electrode. The discharge vessel also has an observation window directly adjacent to the discharge region which is substantially transparent to radiation between ultraviolet and infrared. The dielectric may be quartz, glass, or ceramic. The second electrode may be metallic foil surrounding the discharge vessel adjacent to the first electrode. The discharge region has a partial pressure therein. The partial pressure may be approximately between 1 Torr and atmospheric pressure.

A power supply is electrically connected to the first and second electrodes. The power supply establishes an alternating potential across the first and second electrodes. The amplitude of the alternating potential may be approximately 1-50 kV and the frequency may be approximately 15Hz-3kHz. The alternating potential forms a dielectric barrier discharge within the discharge region that produces active nitrogen. The mean temperature of electrons in the discharge may be approximately between 2-10 eV.

A wavelength sensitive detector coupled to the observation window is utilized to directly measure radiation, from the discharge region, between ultraviolet and infrared of atomic and molecular electronically-excited species generated by the discharge. The wavelength sensitive detector may be an optical filter and a photomultiplier tube. The wavelength sensitive detector may also be a scanning monochromator and a detector. A processor may be operatively connected to the detector for analyzing the spectral characteristics.

In another embodiment, the present invention features an apparatus for monitoring flue gas. The apparatus includes a gas sampler positioned in a flue which is downstream of a combustion chamber. In addition, the apparatus includes a dielectric-barrier discharge vessel for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to atomic and molecular species. The discharge vessel may be formed of quartz, glass, or ceramic tube. Borosilicate glass may also be used.

In addition, the discharge vessel includes an inlet for introducing molecular nitrogen and a sample to be analyzed. The discharge vessel also has an observation window directly adjacent to the discharge region which is substantially transparent to radiation between ultraviolet and infrared. Within the discharge vessel, there exists a discharge region that is defined by a first electrode surrounded by a dielectric and a second electrode. The dielectric may be quartz, glass, or ceramic. The second electrode may be metallic foil surrounding the discharge vessel adjacent to the first electrode. The discharge region has a partial pressure therein. The partial pressure may be approximately between 1 Torr and atmospheric pressure.

A power supply is electrically connected to the first and second electrodes. The power supply establishes an alternating potential across the first and second electrodes. The amplitude of the alternating potential may be approximately 1-50 kV and the frequency may be approximately 15Hz-3kHz. The alternating potential forms a dielectric barrier discharge within the discharge region that produces active nitrogen. The energy of the active nitrogen may be substantially in the Herman infrared spectrum. The mean temperature of electrons in the discharge may be approximately between 2-10 eV.

A wavelength sensitive detector coupled to the observation window is utilized to directly measure, from the discharge region, radiation between ultraviolet and infrared of atomic and molecular electronically-excited species generated by the discharge. The wavelength sensitive detector may be an optical filter and a photomultiplier tube. The wavelength sensitive detector may also be a scanning monochromator and a detector. A processor is utilized for evaluating data from the detector and for controlling combustion in the combustion chamber based upon the evaluation.

Brief Description of the Drawings

The foregoing and other objects, features and advantages of the invention will become apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings. The drawings are not necessarily to scale. Instead emphasis is placed on illustrating the principles of the present invention.

FIG. 1 is a schematic diagram of an active nitrogen energy transfer system for analysis of atomic and molecular species which embodies this invention.

FIG. 2 is a schematic diagram of the dielectric-barrier (DB) discharge vessel described in connection with FIG. 1.

FIG. 3 illustrates a schematic diagram of an apparatus for monitoring flue gas with an active nitrogen energy transfer system which embodies this invention.

FIG. 4a-b illustrates characteristic emission wavelengths for mercury and mercuric chloride obtained using an ANET system which embodies this invention.

Detailed Description

FIG. 1 is a schematic diagram of an active nitrogen energy transfer (ANET) system 10 for analysis of atomic and molecular species which embodies this invention. The ANET system includes a dielectric-barrier discharge vessel 12 for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to the atomic and molecular species. The discharge vessel may be formed of quartz, glass, or ceramic tube. Borosilicate or other high temperature glasses may be used.

The discharge vessel 12 includes an inlet 14 for introducing nitrogen from a molecular nitrogen supply 16 and a sample to be analyzed from a sample source 18. In addition, the discharge vessel 12 includes a gas outlet 20 which is connectable to a vacuum pump (not shown) for controlling the pressure within the discharge vessel 12. Within the discharge vessel 12 there exists a discharge region 22 that is defined by a first electrode 24 and a second electrode 26. The discharge vessel 12 also includes an observation window 28 for directly viewing the discharge region 22. The discharge region 22 has a partial pressure therein which is typically between 1 Torr and atmospheric pressure.

The sample to be analyzed is introduced into the inlet 14 via an input gas line 30. The input gas line 30 is coupled to the molecular nitrogen supply 16 and the sample source 18. A plumbing system 32 is provided for evacuating and purging the input gas line 30.

A power supply 34 is electrically connected to the first 24 and second 26 electrodes. The power supply 34 establishes an alternating potential across the first 24 and second 26 electrodes which generates a dielectric barrier (DB) discharge (not shown). The amplitude of the alternating potential may be approximately 1-50 kV and the frequency may be approximately 15Hz-3kHz. Typically, the power consumed by a DB discharge is typically less than 10 watts.

The DB discharge comprises a multitude of microdischarges that are approximately 100 μm in diameter and that last from 10 to 100 ns. The local current densities are typically in the range of several kA/cm^2. The DB discharge produces active nitrogen containing nitrogen metastables. The use of a dielectric field to impart low-level energy to the nitrogen, so as to raise the energy of the nitrogen to only the Herman infrared region, substantially improves the efficiency over the prior art. In addition, the use of a dielectric avoids sputtering the electrode during electron bombardment and thus avoids spectral interferences resulting from the presence of sputtered material.

The active nitrogen in the Herman infrared spectrum excites only a few strong emissions of each of the sample components. Consequently, the fluorescence spectrum is relatively simple to analyze. Thus, the spectral analysis system used for detecting the fluorescence can be of modest size and resolution. In one embodiment, a scanning monochromator 36 and a detector 38 is coupled to the observation window 28 to directly measure, from the discharge region 22, radiation between ultraviolet and infrared of atomic and molecular electronically-excited species generated by the discharge.

In another embodiment, an optical filter (not shown) and a photomultiplier tube (not shown) may be use to directly measure the radiation. In another embodiment, an optical multichannel analyzer (not shown) and a photomultiplier tube (not shown) may be used to directly measure the radiation. A processor 40 may be connected to the detector 38 for analyzing the spectral characteristics.

FIG. 2 is a schematic diagram of the dielectric-barrier (DB) discharge vessel 12 described in connection with FIG. 1. The discharge vessel 12 is typically formed from one piece of a dielectric material such as quartz, ceramic, or high temperature glass such as borosilicate. The discharge vessel 12 includes an inlet 14 for introducing molecular nitrogen and a sample to be analyzed. The discharge vessel 12 also includes a gas outlet 20 which is connectable to a vacuum pump (not shown) for evacuating the discharge vessel 12. In addition, the discharge vessel 12 includes an observation window 28 for directly viewing the discharge.

The discharge vessel 12 is shaped to form a centrally located gap 50 for supporting the first electrode 24. In addition, the discharge vessel 12 is shaped to form an outer surface 52 suitable for supporting a second electrode 26 that surrounds a portion of the discharge vessel 12. Typically, the portions of the outer surface 52 of the discharge vessel 12, that support the first electrode 24 and the second electrode 26, have a conductive coating 54 such as a graphite or metallic coating.

Within the discharge vessel 12, there exists a discharge region 22 that is defined by the first electrode 24 and the second electrode 26 and that is adjacent to the observation window 28. The first electrode 24 may be a compression fit spiral conducting wire which contacts the conductive coating 54 of the centrally located gap 50. The second electrode 26 may be metallic foil surrounding a portion of the discharge vessel 12 adjacent to the first electrode 24. The foil may be a copper foil. The discharge region 22 has a partial pressure therein which is typically between 1 Torr and atmospheric pressure.

FIG. 3 illustrates a schematic diagram of an apparatus 100 for monitoring flue gas with an active nitrogen energy transfer system which embodies this invention. The apparatus 100 includes a gas sampler 102 positioned in a flue 104 which is coupled to a combustion chamber 106.

The apparatus 100 includes a dielectric-barrier discharge vessel 12 for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to atomic and molecular species. A power supply 34 is electrically connected to the first 24 and second 26 electrodes for generating an alternating potential which forms a DB discharge within the discharge region 22. The energy of the active nitrogen may be substantially in the Herman infrared spectrum.

A scanning monochromator 36 and a detector 38 is coupled to an observation window 28 to directly measure, from the discharge region 22, radiation between ultraviolet and infrared of atomic and molecular electronically-excited species generated by the discharge. A processor 40 is coupled to the detector 38 for evaluating data from the detector 38 and for controlling combustion in the combustion chamber 106 based upon the evaluation. A control panel 42 may also be used to control combustion in the combustion chamber 106.

This invention also features a method for analyzing atomic and molecular species using an ANET system. The method includes providing a dielectric-barrier discharge vessel having a discharge region defined by first and second electrodes. At least one of the first or second electrodes is surrounded by a dielectric material. A partial pressure is established by introducing species to be analyzed and molecular nitrogen into the DB discharge vessel. The species to be analyzed may be particles drawn from contaminated materials into a probe and transported into the vessel. The partial pressure may be approximately between 1 Torr and atmospheric pressure.

An alternating potential is applied across the first and second electrodes. The amplitude of the potential may be approximately 1-50 kV and the frequency may be approximately 15Hz-3kHz. The alternating potential forms a DB discharge that produces active nitrogen. The energy of the active nitrogen may be substantially in the Herman infrared (HIR) spectrum. The mean temperature of electrons in the discharge is approximately between 2-10 eV.

The active nitrogen excites atoms and molecules of the species to be analyzed in the discharge region to emit characteristic emissions. Under steady-state conditions, the species intensity may be given by:

$$I_M{}^* = k_4[M^*] = k_3[M][N_2{}^*].$$

Thus, the fluorescence is linear with [M] and $[N_2{}^*]$, the latter being given by:

$$[N_2{}^*] = k_1[e^-][N_2]/(k_2 + k_3[M] + k_5[Q]).$$

Generally, $k_2 >> k_3[M]$ and $k_5[Q]$; therefore, $[N_2^*]$ is relatively constant. Thus, the observed analyte intensity is linear with species concentration. The linear relationship is advantageous because it simplifies the determination of the species concentration. In addition, the intensity of the HIR increases with pressure from vacuum to atmospheric pressure. Operating the ANET system at atmospheric pressure reduces the complexity of the plumbing system and may eliminate the need for a vacuum pump.

The above method for analyzing atomic and molecular species using an ANET system assumes a steady-state condition. In actual practice, sampling introduces variable concentrations of quenching species which changes $[N_2^*]$ and alters the observed intensity for a given analyte concentration. Since the intensity of the Herman infrared band can be directly correlated with the concentration of the nitrogen metastable, the intensity of the Herman infrared band can be used to correct the analyte intensities for variable quenching.

Exciting the atoms and molecules of the species to be analyzed with active nitrogen is advantageous because the resulting spectra is relatively simple and free of interferences. Thus, the means for detecting the spectral emissions of various species in real time may be less sophisticated than the prior art. The step of detecting the spectral emission may be accomplished with a scanning monochromator and a detector or simply with one or more optical filters optically coupled to one or more photomultiplier tubes.

ANET systems which excite the atoms and molecules of the species to be analyzed with active nitrogen substantially in the Herman infrared spectrum are also highly efficient. The power supplies for such systems may thus be smaller in size, lighter in weight, and less expensive compared with the prior art. Therefore, the ANET system that embodies this invention may be configured to be relatively compact and inexpensive because the system has relatively high efficiency, may operate at atmospheric pressure and thus may not require a vacuum pump, and may produce a relatively simple spectra which is easy to analyze.

Characteristic emissions of the species to be analyzed are directly detected from the discharge region of the discharge vessel. By direct detection we mean coincident excitation, transfer, and detection. Direct detection, at the location where transfer of energy from the metastable exciting species to the species to be analyzed occurs, significantly improves sensitivity compared with the prior art. Direct detection allows for detection of emitted radiation having very low signal-to-noise ratios which may be undetectable downstream due to quenching and radiative loss that occurs in transit from the excitation/transfer region to the detection region.

Therefore, the method of analyzing atomic and molecular species using an ANET system embodying this invention is useful for high sensitivity analysis of both atomic and molecular species of metals, non-metals, and compounds. High sensitivity analysis has been demonstrated for copper, lead, aluminum, silver, nickel, mercury, mercuric chloride, chlorocarbons, hydrocarbons, cadmium, arsenic, selenium, and chromium. The ANET system embodying this invention also may be useful for high sensitivity analysis of numerous other elements including bismuth, bromine, chlorine, germanium, iodine, sulfur, antimony, tin, tellurium, europium, hafnium, magnesium, silicon, thallium, yttrium, zinc, gold, boron, barium, beryllium, calcium, cobalt, cesium, iron, gallium, indium, iridium, lithium, molybdenum, sodium, niobium, phosphorus, palladium, platinum, rhenium, rhodium, strontium, tantalum, thorium, titanium, vanadium, tungsten, zirconium, potassium, and manganese. In addition, the ANET system embodying this invention may be useful for high sensitivity analysis of radioactive elements such as uranium and technetium.

For example, the ANET system embodying this invention may be used for identifying and analyzing wastes for the presence of toxic materials. Specifically, ANET may be utilized to monitor, with a single measurement, the major categories of hazardous waste including transuranic compounds, hydrocarbons, chlorocarbons, and heavy metals. ANET may also be used for detecting dissolved metals in oil including elemental mercury and mercuric chloride, lead, copper, aluminum, silver, and nickel. The ANET system embodying this invention is a more sensitive technique for measuring heavy metals then prior art absorption spectrometry techniques.

FIG. 4a-b illustrates characteristic emission wavelengths for mercury and mercuric chloride obtained by using an ANET system which embodies this invention. The mercury and mercuric chloride were present at parts per billion levels. Experiments have also determined wavelengths that can be used to detect metals such as copper, lead, aluminum, silver, and nickel. In addition, experiments have shown that hydrocarbons will produce CN emission at 388 and 418 nm and will produce CH emission at 431 nm. The ratio of CH to CN may be used to provide an estimate of the C/H ratio of the hydrocarbon.

Equivalents

While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. For example, although the invention is described in connection with a particular dielectric discharge vessel, sample delivery system, and wavelength sensitive detectors, it is noted that other discharge vessels, sample delivery systems, and detectors can be used without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for analyzing atomic and molecular species comprising:

   a) providing a dielectric-barrier discharge vessel comprising a discharge region defined by first and second electrodes, wherein at least one of the first or second electrodes is surrounded by a dielectric material;

   b) establishing a partial pressure by introducing species and molecular nitrogen into the dielectric-barrier discharge vessel;

   c) applying an alternating potential across the first and second electrodes to generate a discharge, thereby producing active nitrogen;

   d) exciting atoms and molecules of the species in the discharge region with the active nitrogen; and

   e) directly detecting characteristic emissions of the species from the discharge region of the discharge vessel.

2. The method of claim 1 wherein the partial pressure is approximately between 1 Torr and atmospheric pressure.

3. The method of claim 1 wherein the step of directly detecting emissions comprises detecting with a scanning monochromator and a detector.

4. The method of claim 1 wherein the step of directly detecting emissions comprises detecting with one or more optical filters optically coupled to one or more photomultiplier tubes.

5. The method of claim 1 wherein the alternating potential across the first and second electrodes has an amplitude of 1-50 kV and a frequency of 15Hz-3kHz.

6. The method of claim 1 wherein the alternating potential across the first and second electrodes generates electrons with mean electron temperatures of between 2-10 eV.

7. A method for analyzing atomic and molecular species comprising:

a) providing a dielectric-barrier discharge vessel comprising a discharge region defined by first and second electrodes, wherein at least one of the first or second electrodes is surrounded by a dielectric material;

b) establishing a partial pressure of between 1 Torr and atmospheric pressure by introducing species and molecular nitrogen into the dielectric-barrier discharge vessel;

c) applying an alternating potential across the first and second electrodes to generate a discharge;

d) producing active nitrogen with energies sufficient to produce Herman infrared emissions from the alternating potential;

e) exciting atoms and molecules of the species in the discharge region with the active nitrogen; and

f) detecting characteristic emissions of the species from the discharge region of the discharge vessel.

8. The method of claim 7 wherein the step of detecting characteristic emissions of the species includes detecting metals, non-metals, and compounds.

9. The method of claim 7 wherein the step of detecting emissions comprises detecting with a scanning monochromator optically coupled to a detector.

10. The method of claim 7 wherein the step of detecting emissions comprises detecting with one or more optical filters optically coupled to one or more photomultiplier tubes.

11. The method of claim 7 wherein the alternating potentials across the first and second electrode has an amplitude of 1-50 kV and a frequency of 15Hz-3kHz.

12. The method of claim 7 wherein the alternating potential across the first and second electrodes generates electrons with mean electron temperatures of between 2-10 eV.

13. An apparatus for analysis of atomic and molecular species comprising:

a) a dielectric-barrier discharge vessel for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to the atomic and molecular species comprising:

i) a discharge region within the discharge vessel defined by a first electrode surrounded by a dielectric and a second electrode, the discharge region having a partial pressure therein;

ii) an inlet for introducing molecular nitrogen and a sample to be analyzed into the discharge vessel; and

iii) an observation window directly adjacent the discharge region and substantially transparent to radiation between ultraviolet and infrared;

b) a power supply electrically connected to the first and second electrodes;

c) a dielectric barrier discharge within the discharge region, wherein the discharge is generated by the power supply; and

d) a wavelength sensitive detector coupled to the observation window for directly measuring, from the discharge region, radiation between ultraviolet and infrared of atomic and molecular electronically-excited species generated by the discharge.

14. The apparatus of claim 13 wherein the partial pressure is approximately between 1 Torr and atmospheric pressure.

15. The apparatus of claim 13 wherein the power supply establishes an electrical field in the discharge region which generates electrons with mean temperatures of between 2-10 eV.

16. The apparatus of claim 13 wherein the second electrode is a metallic foil surrounding the discharge vessel adjacent to the first electrode.

17. The apparatus of claim 13 wherein the power supply generates a potential difference between the first and second electrodes of 1-50 kV at a frequency of 15Hz-3kHz.

18. The apparatus of claim 13 wherein the dielectric comprises quartz, glass, or ceramic.

19. The apparatus of claim 13 wherein the discharge vessel comprises quartz, glass, or ceramic tube.

20. The apparatus of claim 13 wherein the wavelength sensitive detector comprises an optical filter and a photomultiplier tube.

21. The apparatus of claim 13 wherein the wavelength sensitive detector comprises a scanning monochromator and a detector.

22. The apparatus of claim 21 further comprising a processor operatively connected to the detector for analyzing the spectral characteristics.

23. An apparatus for monitoring flue gas, comprising:

a) a gas sampler positioned in a flue coupled to a combustion chamber;

b) a dielectric-barrier discharge vessel for exciting molecular nitrogen in a nitrogen-containing gas to a plurality of nitrogen metastable excited states and for transferring energy from the excited states to atomic and molecular species comprising:

i) a discharge region within the discharge vessel defined by a first electrode surrounded by a dielectric and a second electrode, the discharge region having a partial pressure therein;

ii) an inlet for introducing molecular nitrogen and flue gas from the gas sampler into the discharge vessel; and

iii) an observation window adjacent the discharge region and substantially transparent to radiation between ultraviolet and infrared;

c) a power supply electrically connected to the first and second electrodes;

d) a dielectric barrier discharge within the discharge region, wherein the discharge is generated by the power supply;

e) a wavelength sensitive detector coupled to the observation window for directly measuring, from the discharge region, radiation between ultraviolet and infrared of atomic and molecular electronically-excited states generated by the discharge.

f) a processor for evaluating data from the detector and for controlling combustion in the combustion chamber based upon the evaluation.

24. The apparatus of claim 23 wherein the discharge produces active nitrogen with energies sufficient to produce Herman infrared emissions.

25. The apparatus of claim 23 wherein the partial pressure is approximately between 1 Torr and atmospheric pressure.

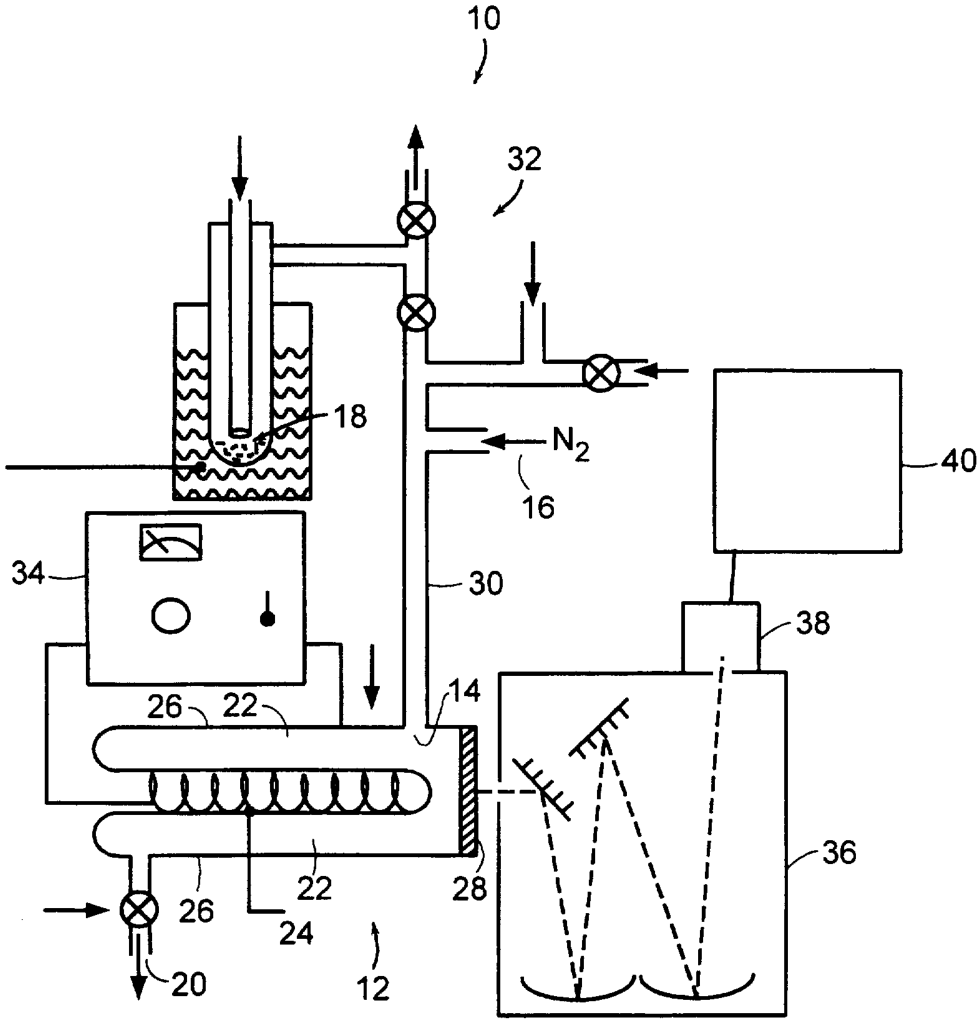

FIG. 1

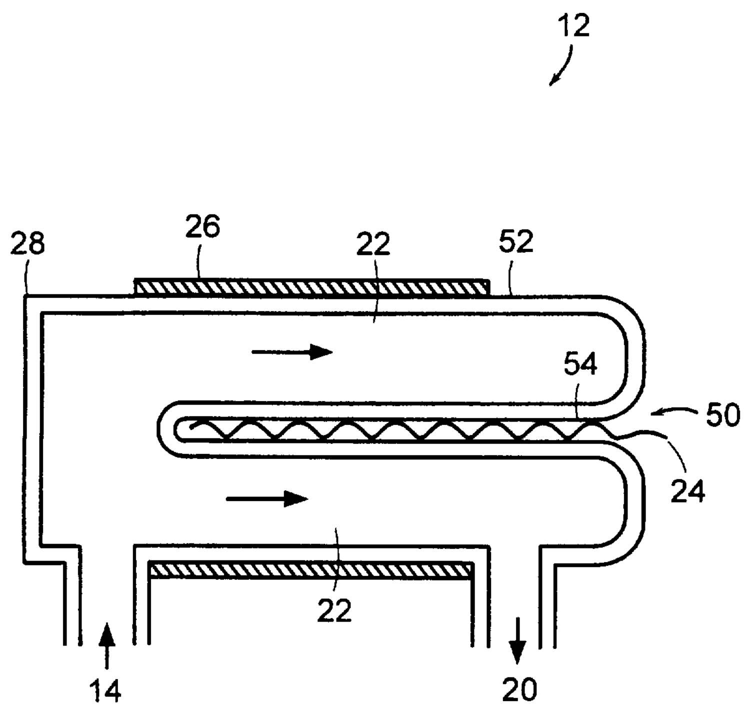

FIG. 2

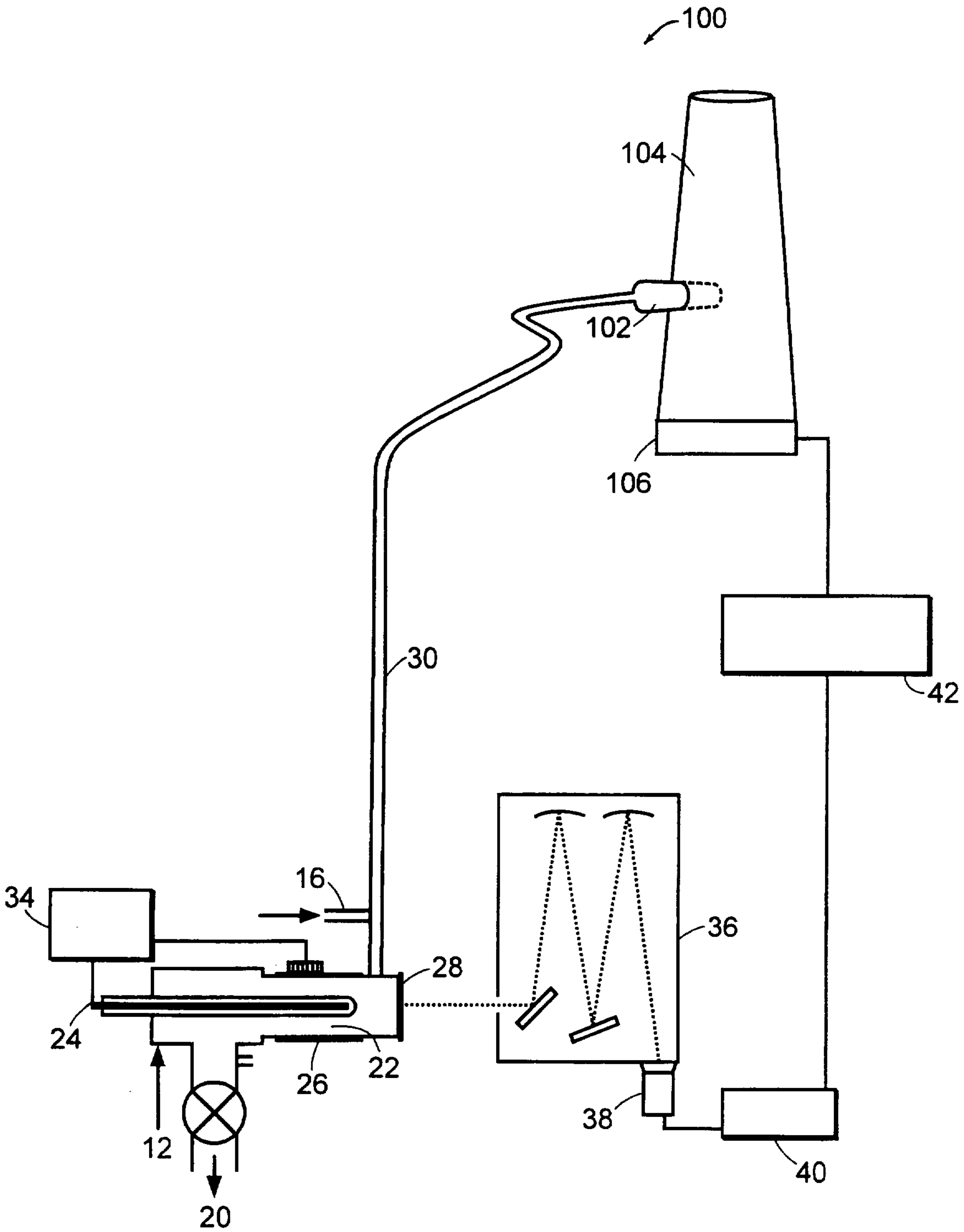

FIG. 3

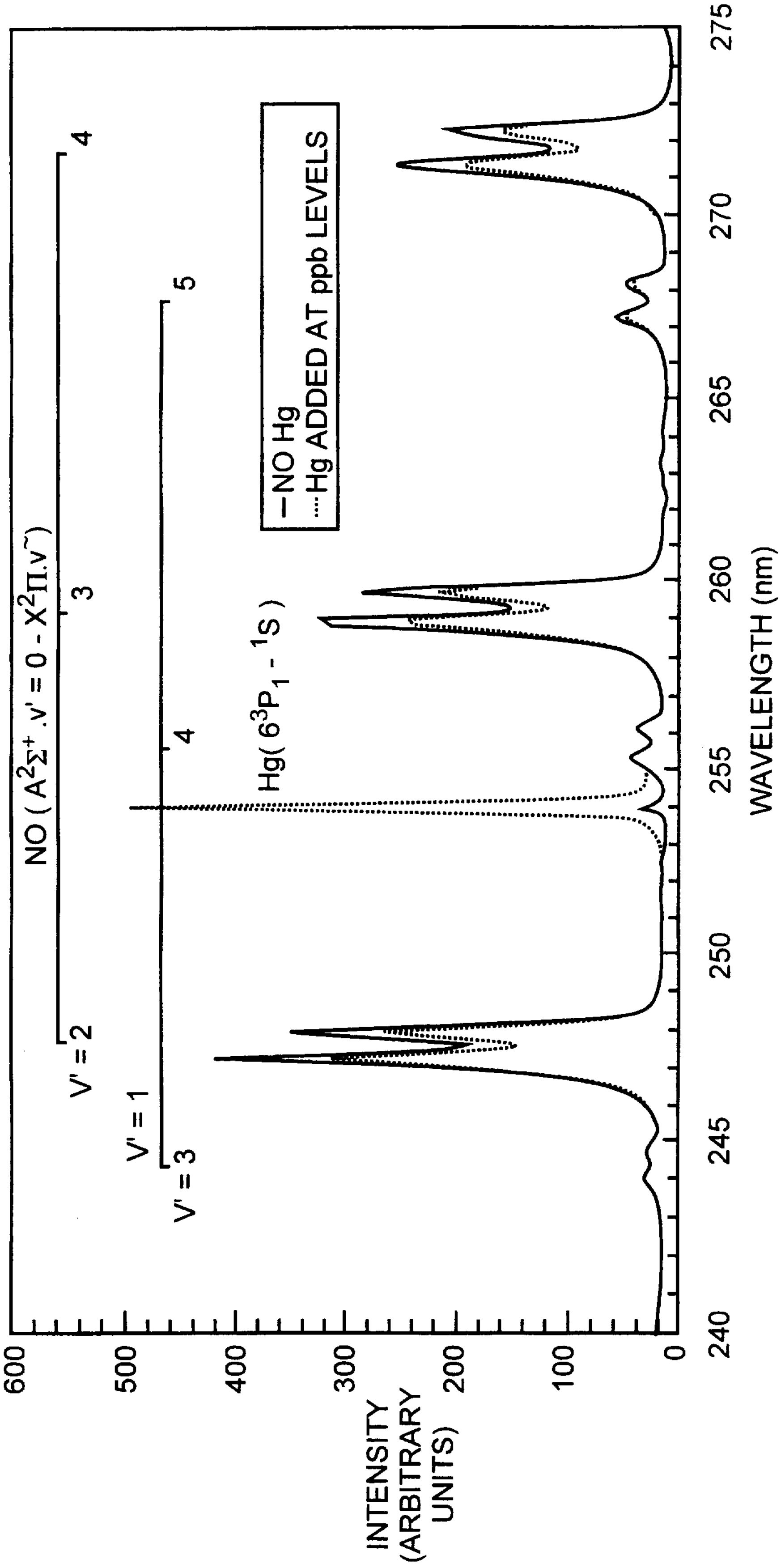
INTENSITY
(ARBITRARY
UNITS)
0
100
200
300
400
500
600
240
245
250
255
260
265
270
275
WAVELENGTH (nm)
NO ($A^2\Sigma^+ . v' = 0 - X^2\Pi . v''$)
V' = 2
3
4
V' = 1
V' = 3
4
5
$Hg(6^3P_1 - {}^1S)$
—NO Hg
····Hg ADDED AT ppb LEVELS

FIG. 4A

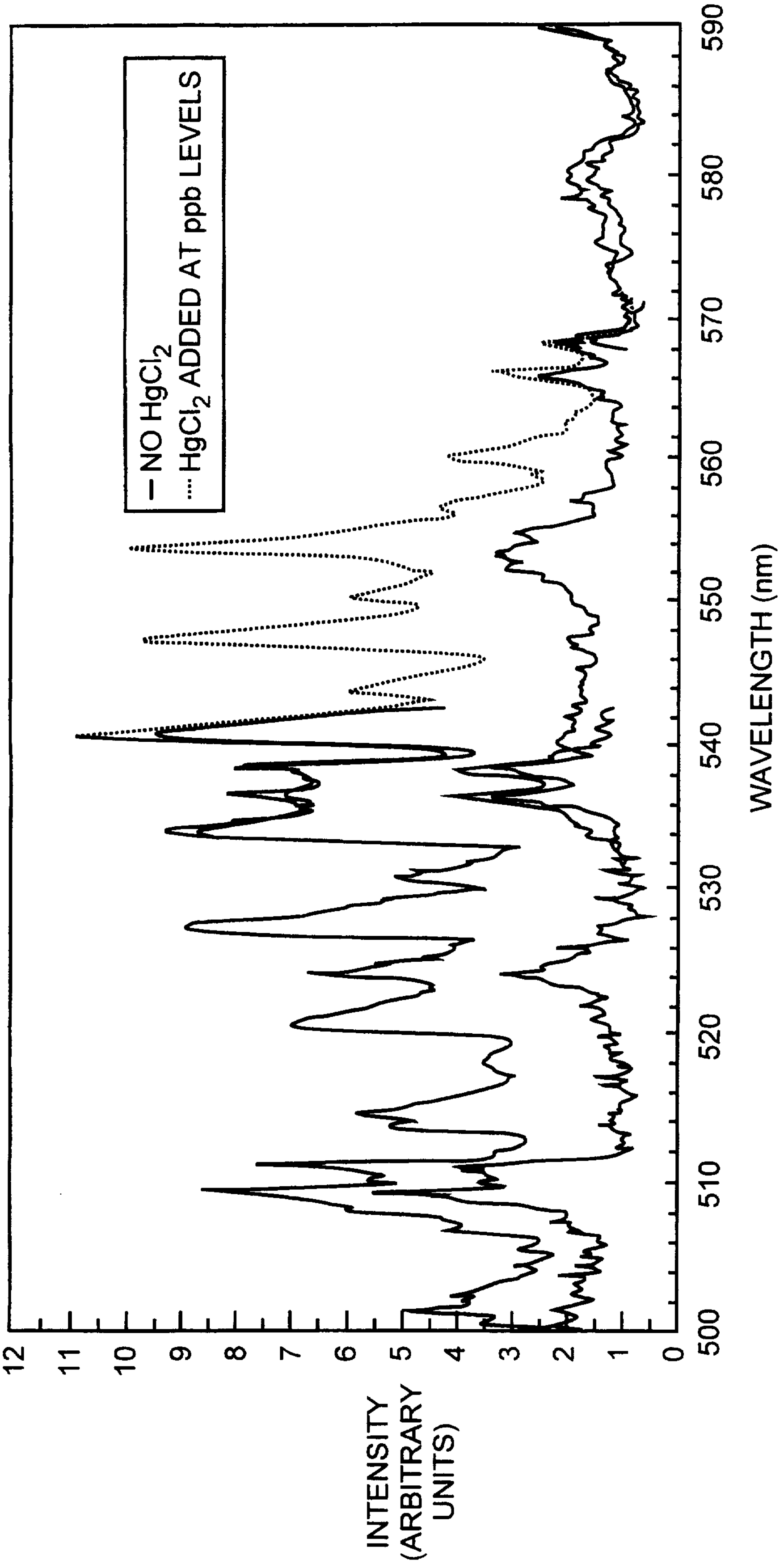
— NO $HgCl_2$
···· $HgCl_2$ ADDED AT ppb LEVELS
INTENSITY (ARBITRARY UNITS)
0
1
2
3
4
5
6
7
8
9
10
11
12
WAVELENGTH (nm)
500
510
520
530
540
550
560
570
580
590

FIG. 4B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/01447

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/62

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)
IPC 6 G01N

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 practical, 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.
A	US 4 309 187 A (DODGE III WILLIAM B ET AL) 5 January 1982 see the whole document ---	1-23,25
A	APPLIED SPECTROSCOPY, vol. 34, no. 5, 1980, BALTIMORE US, pages 578-584, XP002031776 A.P.D'SILVA ET AL.: "Atmospheric Pressure Active Nitrogen (APAN) - A New Source for Analytical Spectroscopy" see page 578 - page 580 -----	1-5,7, 9-11,13, 14, 16-23,25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"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

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
28 May 1997	06.06.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Scheu, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati Application No
PCT/US 97/01447

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4309187 A	05-01-82	NONE	