The present invention provides an analysis method and analysis apparatus for a sulfur component using ultraviolet fluorescence capable of removing the interferential influence of NO with good efficiency and certainty to thereby measure a concentration of only sulfur components such as SO₂ and others even in continuous measurement over a long term with a high precision.

The present invention is an analysis method for a sulfur component using ultraviolet fluorescence in which a sample gas is illuminated with ultraviolet and fluorescence emitted by the ultraviolet illumination is detected to measure concentrations of sulfur components including at least SO₂ in the sample gas, wherein NO, which is an interferential component in the sample gas, is oxidized to nitrogen dioxide, followed by illuminating the sample gas with ultraviolet.
[0001] The present invention relates to an analysis method for a sulfur component using ultraviolet fluorescence adopted for measuring concentrations of sulfur components including sulfur dioxide (hereinafter referred to as SO2) in a sample gas such as, for example, an automobile emission, and an analysis apparatus used in conducting the method.

[0002] A nondispersive infrared gas analysis method (NDIR method) has conventionally been adopted in general aspects as a measuring method for concentrations of sulfur components such as SO2 in a sample gas such as an automobile emission, whereas in the NDIR method, an inconvenience could not be avoided that even if an optical filter is used, because of a low removal percentage of interferential components such as H2O and HC coexisting with a sulfur component as a measurement objective in a sample gas, the interferential components give an adverse influence on a measurement precision. In order to eliminate the adverse influence caused by such interferential components, which is hereinafter simply referred to as interferential influence, a necessity arises for installing a greatly expensive pretreatment facility, leading to complexity and scaling-up of the apparatus in the entirety in which H2O is removed using a Perma-pure drier (PPD) and HC is removed by burning it to convert to CO2 in a high temperature combustion furnace at a temperature in the vicinity of 900°C with an oxidation catalyst. Even in a case where such a pretreatment facility is installed, the interferential influence cannot be perfectly removed; therefore, in addition to the pretreatment facility, another necessity arises for eliminating the interferential influence, for example, by adopting a so-called fluid modulation method (cross-flow) in which a sample gas and a reference gas are alternately introduced into a sample cell at a given period in a given amount, resulting in faults due to not only further increasing a facility cost and scaling-up of the apparatus, but also lacking responsiveness to a sudden change in concentration of a gas to be measured to thereby cause a transient error and in turn, to disable high measurement precision to be obtained.

[0003] As a measuring method for a sulfur component concentration as a replacement for the NDIR method having faults in facility cost and in measurement precision caused by responsiveness to a sudden change in concentration, an analysis method for a sulfur component based on ultraviolet fluorescence has conventionally been already known in which a sample gas is illuminated with ultraviolet to detect an intensity of fluorescence caused by the ultraviolet illumination and measure concentrations of sulfur components including SO2 in the sample gas. Although an analysis method for a sulfur component using ultraviolet fluorescence has a higher ability in selectively measuring only sulfur components such as SO2 to be measured as compared with other analysis methods such as the NDIR method, included in a sample gas are nitrogen monoxide (hereinafter referred to as NO) emitting fluorescence in a similar way to that a sulfur component to be measured, especially SO2, and NO works as an interferential component in measurement of SO2, leading to a severe interferential influence to be received.

[0004] To be detailed, in a case of an analysis method for a sulfur component using ultraviolet fluorescence, while illumination is conducted with ultraviolet having a selected wavelength in the vicinity of 220 nm in measurement of SO2, NO included in a sample gas as an interferential component has narrow isolated absorption wavelength regions in the vicinities of wavelengths of 214 nm and 226 nm, which are extremely close to an ultraviolet wavelength for exciting SO2, and fluorescence spectra of SO2 and NO overlap each other to thereby detect an intensity of fluorescence emitted from NO together with that from SO2, resulting in a problem that NO exerts a conspicuous interferential influence on measurement on SO2, which leads to a measurement error.

[0005] As an eliminating means for the interferential influence caused by NO, there has been conventionally available a gas filter scheme in which a wavelength selecting section including a gas filter, in which NO is sealed, selectively absorbing light in the vicinities of wavelengths of 214 nm and 226 nm, is installed in an optical path between a light source emitting ultraviolet and a sample chamber of an ultraviolet fluorometric analyzer not to thereby cause NO to be excited and fluoresce (see, for example, JP Publication No. 11-183385).

[0006] A subtraction method has been proposed in which provided are: a sample chamber into which a sample gas including SO2 and NO is introduced; and a sample chamber into which a sample gas is introduced by way of a mechanism to remove SO2 with active charcoal; and in addition, two light sources emitting ultraviolet to respective both sample chambers; and two detection sections detecting fluorescence in respective both chamber, wherein a fluorescence amount detected in the latter sample chamber is subtracted from a fluorescence amount detected in the former sample chamber to thereby obtain a fluorescence amount only from SO2 including no interferential influence caused by NO because of the removal (see JP Publication No. 7-63683).

[0007] In a case of the gas filter scheme, however, among the above conventional NO interferential influence removal

Description of the Prior Art

Field of the Invention

BACKGROUND OF THE INVENTION

EP 2 182 344 A1
means, an absorption ability of a selected wavelength is reduced by chronological changes in property, condition or the
like of a sealed NO gas, and the interferential influence of NO cannot be fully removed through continuous measurement
over a long term, which gives birth to a possibility to cause a measurement error, thereby having left an improvement
to be in an aspect of measurement precision in continuous measurement use. In a case of the subtraction method, not
only two sets of a sample chamber, a light source and a detection section necessary to be installed, but an arithmetic
circuit operating a subtraction is also required, therefore, having led to a problem of complexity and cost-up of the
apparatus in the entirety, and furthermore, it takes a considerable time in removal of the interferential influence by
applying a subtraction operation on both fluorescence amounts after both fluorescence amounts detected in the two
sample chambers are stored and held, having led to another problem of poor measurement efficiency for a SO$_2$

[0008] The present invention has been made in light of the above described circumstances and it is an object of the
present invention to provide an analysis method and analysis apparatus for a sulfur component using ultraviolet fluo-
rescence capable of removing the interferential influence of NO with good efficiency and certainty to thereby measure
a concentration of only sulfur components such as SO$_2$ and others even in continuous measurement over a long term
with a high precision.

SUMMARY OF THE INVENTION

[0009] An analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention
in order to achieve the object is directed to an analysis method for a sulfur component using ultraviolet fluorescence in
which a sample gas is illuminated with ultraviolet and fluorescence emitted by the ultraviolet illumination is detected to
measure concentrations of sulfur components including at least SO$_2$ in the sample gas, wherein NO, which is an inter-
ferential component in the sample gas, is oxidized to nitrogen dioxide (hereinafter referred to as NO$_2$), followed by
illuminating the sample gas with ultraviolet.

[0010] An analysis apparatus for a sulfur component using ultraviolet fluorescence pertaining to the present invention
in order to achieve the same object as in the above description is directed to an analysis apparatus for a sulfur component
using ultraviolet fluorescence including: an introducing pipe for a sample gas; and an ultraviolet fluorometric analyzer,
connected to the introducing pipe, and illuminating the sample gas with ultraviolet to detect fluorescence emitted ac-
companying the illumination and to thereby measure concentrations of sulfur components including at least SO$_2$ in the
sample gas, wherein means oxidizing NO, which is an interferential component in the sample gas, to NO$_2$ is installed
in the introducing pipe part way downstream from the inlet end thereof or immediate after the introducing pipe.

[0011] According to an analysis method and analysis apparatus for a sulfur component using ultraviolet fluorescence
pertaining to the present invention with features as described above, NO, which is the interferential component included
in the sample gas, is oxidized to NO$_2$ exerting no interferential influence before fluorescence emitted by illumination of
the sample gas with ultraviolet is detected; therefore, a concentration of only sulfur components such as SO$_2$ and others
to be measured can be obtained without the interferential influence of NO to be exerted. Since the interferential influence
of NO is removed by oxidation (transformation) of NO to NO$_2$, there occurs absolutely no adverse possibility of incomplete
or uncertain removal of the interferential influence due to reduction in absorption power for a selected wavelength caused
by chronological changes in property and condition of NO gas, which has been experienced in a conventional gas filter
scheme, thereby enabling the interferential influence of NO to be removed with certainty even in continuous measurement
over a long term to measure concentrations of only sulfur components such as SO$_2$ and others with a high precision at
all times. An effect can be exerted that a construction is much simpler as compared with that of the conventional
subtraction method; therefore, not only can the apparatus in the entirety be more compact and of lower cost, but the
interferential influence of NO can also be removed with good efficiency to thereby greatly improve efficiencies in meas-
urement and analysis of concentrations of a particular sulfur component.

[0012] Especially, it is desirable in the present invention to adopt means adding ozone into a sample gas as described
in claim 2 and claim 4 as means oxidizing NO to NO$_2$. In this case, an added amount of ozone is controlled according
to a change in a NO concentration, which is an interferential component, to thereby enable all NO to be oxidized to NO$_2$
with good efficiency through a reaction of NO included in the sample gas with ozone, and occurrence of measurement
error caused by the interferential influence can be prevented irrespectively of a change in concentration, thereby enabling
high precision measurement to be conducted at all times.

[0013] In an analysis apparatus for a sulfur component using ultraviolet fluorescence pertaining the present invention,
there is provided heating means heating to and holding at a temperature in the introducing pipe of the sample gas and
the sample chamber of the ultraviolet fluorometric analyzer in the range where no moisture in the sample is at least
condensed to thereby enable condensation of moisture in the sample gas and adsorption of the sulfur components to
be prevented, leading to more of improvement on measurement precision of concentrations of sulfur components such
as SO$_2$.

[0014] In an analysis apparatus for a sulfur component using ultraviolet fluorescence pertaining to the present invention,
as described in claim 6, a pretreatment section having a first gas line and a second gas line and a valve changing over between flows of the sample gas into the first and second gas lines may be provided immediately prior to the ultraviolet fluorometric analyzer, and means oxidizing a sulfur compound in the sample gas to sulfur dioxide may be provided in the first gas line. In this case, a flow of the sample gas is changed over into the first gas line to thereby oxidize sulfur compounds such as H₂S, CS₂ and others in the sample gas to SO₂ and to enable a concentration of all the sulfur components in the sample gas to be measured, while on the other hand, being changed over into the second gas line not to thereby oxidize the sulfur compounds such as H₂S, CS₂ and others to SO₂ and to therefore, enable a concentration of only SO₂ actually included in the sample gas to be measured, so that measurements on concentrations of sulfur components can be individually conducted by changing over between two kinds thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 is a view showing an outline of construction of an analysis apparatus in the entirety according to a first embodiment adopting an analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention;

Fig. 2 is a view showing an outline of construction of an analysis apparatus in the entirety according to a second embodiment adopting an analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention; and

Fig. 3 is an enlarged sectional view showing a main part structure of construction of an analysis apparatus according to a third embodiment adopting an analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] Description will be given of an embodiment of the present invention below with reference to the accompanying drawings.

[0017] Fig. 1 is a view showing an outline of construction of an analysis apparatus in the entirety according to a first embodiment adopting an analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention. In the figure, a numerical symbol 1 indicates an introducing pipe introducing a sample gas G such as automobile exhaust gas into an ultraviolet fluorometric analyzer 2; and a physical filter 3 removing foreign matter mixed in the sample gas G and a flow rate adjusting valve 4 are inserted in series in the introducing pipe 1 part way downstream from the inlet end thereof. An ozone (hereinafter referred to O₃) supply pipe 6 to which a flow rate adjusting valve 25 capable of adjusting a flow rate of O₃ generated from pure oxygen (hereinafter referred to O₂) in an ozone generator 5 is attached is communication-connected to the introducing pipe 2 at a site downstream from the flow rate adjusting valve 4, and O₂ is added and mixed into the sample gas G flowing in the introducing pipe 1 through the supply pipe 6 to thereby constitute a means oxidizing NO included in the sample gas G to NO₂ through a reaction with O₃.

[0018] Note that not only is a by-pass pipe 7 discharging the excessive sample gas to the outside connected to the introducing pipe 1 as a branch, but also provided part way downstream from the branching connection of a supply tube 8 is an automatic control valve 9 automatically adjusted with respect to an opening level thereof based on a measured gas flow rate in the supply pipe 6 for O₃, wherein by adjustment in an opening degree of the automatic control valve 8, a flow rate of the sample gas G flowing in the introducing pipe 1, and a flow rate of O₃ added and mixed into the sample gas G through the supply pipe 6 are controlled at a constant ratio at all times.

[0019] The ultraviolet fluorometric analyzer 2 includes: a sample chamber (cell) into which introduced are the sample gas including NO₂ obtained by oxidation of NO and sulfur components such as SO₂ to be measured; a light source illuminating the interior of the cell with ultraviolet having a wavelength in the vicinity of 220 nm, and a detector detecting a fluorescent intensity selecting, using an optical filter, fluorescence having a wavelength in the vicinity of 330 nm obtained by excitation caused by ultraviolet illumination; and others, which construction is well known; therefore, the construction is not shown in a concrete way and description thereof is also omitted.

[0020] The introducing pipe 1 for the sample gas G and the cell of ultraviolet fluorometric analyzer 2 obliquely hatched in Fig. 1 are heated to and held at a temperature at all times by a heating means such as an electrical heater. The heating means is constructed so that a temperature of the sample gas G is controlled in the range of from 110°C to 120°C at which neither a moisture in the sample gas G is condensed and nor an S compound is adsorbed by current control means is constructed so that a temperature of the sample gas G is controlled in the range of from 110°C to 120°C.

[0021] A deozonator 11 decomposing O₃ and a drain separator 12 are attached to an exhaust pipe extending from the cell of the ultraviolet fluorometric analyzer 2, and a drain pot 13 and a drain pipe 15 with an opening/closing valve.
Then, description will be given of a method for measuring and analyzing a concentration of SO\textsubscript{2} included in the sample gas G using ultraviolet fluorescence with the analysis apparatus of the first embodiment constructed as described above. If O\textsubscript{3} generated by the ozone generator 5 is added and mixed into the sample gas G including sulfur components such as SO\textsubscript{2} to be measured and NO, which is an interferential component, introduced into the introducing pipe 1 and flowing therein, at a constant ratio through the supply pipe 6, NO in the sample gas G reacts with O\textsubscript{3} to be oxidized to NO\textsubscript{2} and thereafter the sample gas G including NO\textsubscript{2} obtained by oxidation is introduced into the cell of the ultraviolet fluorometric analyzer 2. In this situation, the introducing pipe 1 for the sample gas G and the cell of the ultraviolet fluorometric analyzer 2 are heated by means of a heating means such as an electrical heater and further controlled at a temperature in the range of from 110°C to 120°C by current control or the like based on a detected temperature by the thermocouple 9; therefore, neither a moisture in the sample gas G is condensed nor an S compound is adsorbed. Therefore, when the interior of the cell is illuminated with ultraviolet having a wavelength in the vicinity of 220 nm emitted from the light source, only SO\textsubscript{2} in the sample gas G is excited and then, the excited SO\textsubscript{2} is relaxed to emit fluorescence having a wavelength in the vicinity of 330 nm. The fluorescence having a wavelength in the vicinity of 330 nm selectively passes through the optical filter to detect a fluorescent intensity by a detector and the detected fluorescent intensity is quantified as an numeral using a calibration curve prepared in advance, thereby enabling a concentration of SO\textsubscript{2} included in automobile emission or the like is measured and analyzed with a high precision in a state where no interferential influence is exerted by NO, H\textsubscript{2}O or the like included in the sample gas G.

Incidentally, in Table 1, there are shown interferential influence values due to various kinds of gases included in a sample gas G when O\textsubscript{3} is added and interferential influence values due to NO in a sample gas G when no O is added (in value expressed in terms of SO\textsubscript{2} output), and when O\textsubscript{3} is added, an interferential influence value equal to or less than a detection limit was obtained on any of a gas component included. It is also clearly shown in Table 1 that an interferential influence caused by NO, which is the largest interferential component in measurement of an SO\textsubscript{2} concentration using ultraviolet fluorescence when O\textsubscript{3} is added is equal to or less than the detection limit.

![Table 1](image)

Table 1

<table>
<thead>
<tr>
<th>kind of gas</th>
<th>concentration</th>
<th>result of interferential influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>4788 ppm</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>228 ppm</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>6.53 vol%</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>343.7 ppm</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>CO</td>
<td>8.396 vol%</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>17.18 vol%</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>3273 ppm</td>
<td>equal to or less than detection limit</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>20.7 vol%</td>
<td>equal to or less than detection limit</td>
</tr>
</tbody>
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when O\textsubscript{3} is not added

<table>
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<tr>
<th>kind of gas</th>
<th>concentration</th>
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</thead>
<tbody>
<tr>
<td>NO</td>
<td>95.66 ppm</td>
<td>49ppm\textsuperscript{(1)}</td>
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</table>

![Fig. 2](image)

Fig. 2 is a view showing an outline of construction of an analysis apparatus in the entirety according to a second embodiment adopting an analysis method for a sulfur component using ultraviolet fluorescence pertaining to the present invention. In the analysis apparatus according to the second embodiment, the construction is the same as in the first embodiment with the exception that a pretreatment section 16 described below is provided just before the ultraviolet fluorometric analyzer 2 and the same symbols are attached to the corresponding constituents and detailed descriptions thereof are omitted.

The pretreatment section 16 includes: a quartz tube 17 having an oxidation catalyst (CAT) made from a ceramic such as vanadium pentoxide or mulite (Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}) with a high content of silicon oxide (SiO\textsubscript{2}) therein; a filter 21; a first gas line 18 constructed so as to control a heating temperature of the quartz tube 17 at a temperature of the order of
In a case where the analysis apparatus of the second embodiment constructed as described above is used to measure and analyze concentrations of sulfur components such as SO$_2$ and others included in the sample gas G using ultraviolet fluorescence, if the valves 23 and 24 are changed over in order to cause the sample gas G to flow in the first gas line 18 of the pretreatment section 16, sulfur compounds such as H$_2$S and CS$_2$ in the sample gas are oxidized to SO$_2$ while the sample gas G passes through the quartz tube 17 and then introduced into the cell of the ultraviolet fluorometric analyzer 2, where a concentration of all the sulfur components in the sample gas are measured, while if the valves 23 and 24 are changed over in order to cause the sample gas G to flow in the second gas line 20 of the pretreatment section 16, sulfur compounds such as H$_2$S and CS$_2$ in the sample gas are not oxidized to SO$_2$ while the sample gas G passes through the dummy pipe 19 and, as they are, introduced into the cell of the ultraviolet fluorometric analyzer 2, where a concentration of only SO$_2$ in the sample gas are measured. That is, only by changing over between the first and second lines 18 and 20 in the pretreatment section 16, the apparatus can be used changing over between the two kinds of measurement of a concentration of all the sulfur components in the sample gas and a concentration of only SO$_2$ in the sample gas at any time with simplicity.

Incidentally, in Table 2, there are shown relative sensitivities when each of various kinds of sulfur compounds such as H$_2$S and CS$_2$ is measured using the first gas line 18 and the values of the sensitivities, when that of SO$_2$ as a reference (1.0) is used, are 0.9 or larger on all sulfur components: it is clear from Table 2 that a measurement precision is high for all the sulfur components.

<table>
<thead>
<tr>
<th>name of compound</th>
<th>relative sensitivity</th>
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<tbody>
<tr>
<td>SO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.99</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>CH$_3$SH</td>
<td>0.98</td>
</tr>
<tr>
<td>C$_2$H$_4$S</td>
<td>1.00</td>
</tr>
<tr>
<td>(CH$_3$)$_2$S</td>
<td>1.00</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_2$S</td>
<td>1.00</td>
</tr>
<tr>
<td>COS</td>
<td>0.91</td>
</tr>
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Note that while in the above described embodiments, a means in which O$_3$ is added and mixed into the sample gas G is used as a means to oxidize NO to NO$_2$, another construction may be adopted in which O$_2$ is added into the sample gas G, which is illuminated with ultraviolet from the light source of the ultraviolet fluorometric analyzer 2, thereby oxidizing NO in the sample gas G to NO$_2$.

Fig. 3, which shows detailed structure of above construction, is a sectional view of the vicinity of the ultraviolet fluorometric analyzer 2, and in a sample chamber (cell) 28 having an introducing section 26 and a discharging section 27 for the sample gas G, there is integrally provided, as a single piece therewith, a detector 31 such as a photodiode selecting only fluorescence having a wavelength in the vicinity of 330 nm emitted from SO$_2$ through a fluorescence collective lens 29 and through an optical filter 30 to detect an intensity thereof; in addition, sideways to the outside of the cell 28 in the sample gas introducing section 26 side, there is installed an ultraviolet lamp (light source) 34 emitting ultraviolet directed to the sample gas in the cell 28 through excitation collective lens 32 and through an optical filter 33; and to a site close to the sample gas introducing section 26 of the introducing pipe 1, there is communication-connected an O$_2$ supply pipe 35.

In an analysis apparatus for a sulfur component using ultraviolet fluorescence, constructed as shown in Fig. 3, the sample gas G added and mixed with O$_2$ at a given ratio through the supply pipe 35 is introduced into the cell 28 through the introducing section 26 and the O$_2$ mixed sample gas G is illuminated with ultraviolet not only to thereby cause NO in the sample gas G to react with O$_2$ to NO$_2$ in an oxidized form but also to excite NO$_2$ and SO$_2$ in the sample gas G including NO$_2$ obtained by oxidation with the result that emission of fluorescence therefrom. Only fluorescence having a wavelength in the vicinity of 330 nm of all the fluorescence is selectively detected by the detector 31 through the collective lens 29 and the optical filter 30, thereby enabling a fluorescent intensity of SO$_2$, that is a concentration of...
SO₂ to be measured and analyzed with a high precision without receiving an interferential influence caused by NO. [0031] In the second embodiment shown in Fig. 2, by adding a pretreatment apparatus such as a scrubber for SO₂ to a gas introducing section to the cell of ultraviolet fluorometric analyzer 2, a concentration of sulfur components except for SO₂ can be measured when the first gas line 18 is used by changeover and furthermore, by adding another pretreatment apparatus using active charcoal or a high temperature furnace at 1000°C or higher, a concentration of SO₃ or the like can also be measured.

[0032] Further embodiments are:

1. A method for analyzing sulfur components, including sulfur dioxide (SO₂), in a sample gas (G) containing nitrogen monoxide (NO), comprising illuminating said sample gas with ultraviolet light and detecting of fluorescence to measure said sulfur components, including SO₂, characterized in that said NO is oxidized to nitrogen dioxide (NO₂) before said detecting of fluorescence.

2. The method according to item 1, wherein said NO is oxidized to NO₂ by adding ozone (O₃) into said sample gas.

3. The method according to item 1, wherein said NO is oxidized to NO₂ by adding oxygen (O₂) into said sample gas, followed by said illuminating said sample gas (G) with ultraviolet light.

4. The method according to one of the items 1 to 3, wherein said sample gas is heated to a temperature selectively chosen to avoid condensing of moisture in said sample gas (G).

5. The method according to item 4, wherein said sample gas (G) is heated to a temperature in the range of from 110°C to 120°C.

6. The method according to one of the items 1 to 5, wherein, before said detecting of fluorescence of said sample gas, said sample gas is pretreated to oxidize said sulfur compounds to sulfur dioxide (SO₂).

7. An apparatus for analyzing sulfur components, including sulfur dioxide (SO₂), in a sample gas using ultraviolet fluorescence, which comprises an introducing pipe (1) for introducing a sample gas (G) connected to said introducing pipe (1), an ultraviolet fluorometric analyzer (2) for detecting said sulfur components, characterized in that said apparatus comprises means for oxidizing nitrogen monoxide (NO) to nitrogen dioxide (NO₂) before detecting said sulfur components.

8. The apparatus according to item 7, wherein said means for oxidizing nitrogen monoxide (NO) to nitrogen dioxide (NO₂) is a means for adding ozone (O₃) into said sample gas (G).

9. The apparatus according to item 7 or 8, further comprising a heating means for heating said sample gas (G) in said introducing pipe and said fluorometric analyzer (2) to a temperature, where no moisture in said sample gas is condensed.

10. The apparatus according to one of the items 7 to 9, further comprising a pretreatment section (16) provided upstream of said fluorometric analyzer (2), said pretreatment section having a first gas line (18) and a second gas line (20) and a valve (22) for changing over flows of said sample gas (G) into said first or second gas lines, said first gas line being provided with means for oxidizing said sulfur components in said sample gas to sulfur dioxide (SO₂).

Claims

1. An apparatus for analyzing sulfur components, including sulfur dioxide, in a sample gas (G) using ultraviolet fluorescence, comprising:

   an introducing pipe (1) for introducing a sample gas (G),
   an ultraviolet fluorometric analyzer (2) for detecting said sulfur components and connected to said introducing pipe (1),
   a pretreatment section (16) provided upstream of said fluorometric analyzer (2), said pretreatment for oxidizing said sulfur components other than sulfur dioxide (SO₂) in said sample gas (G) to sulfur dioxide (SO₂), and
means (5, 25, 6) for oxidizing nitrogen monoxide (NO) to nitrogen dioxide (NO₂) before detecting said sulfur components, being installed in said introducing pipe (1) downstream from an inlet end thereof or immediate after the introducing pipe (1), and being configured such that an oxidation gas (O₃, O₂) is added and mixed into the sample gas (G) while controlling the flow rate of the oxidation gas (O₃, O₂) and the flow rate of the sample gas (G) at a constant ratio at all times.

2. A method for analyzing sulfur components, including sulfur dioxide (SO₂), in a sample gas (G) containing nitrogen monoxide (NO), comprising:

   illuminating said sample gas (G) with ultraviolet light and
detecting of fluorescence to measure said sulfur components, including sulfur dioxide (SO₂),

wherein:

   an oxidation gas (O₃, O₂) is added and mixed into the sample gas (G) while controlling the flow rate of the oxidation gas (O₃, O₂) and the flow rate of the sample gas (G) at a constant ratio at all times,
said nitrogen monoxide (NO) is oxidized to nitrogen dioxide (NO₂) before said detecting of fluorescence,
sulfur components other than sulfur dioxide (SO₂) are oxidized to sulfur dioxide (SO₂) before said detecting of fluorescence of said sample gas (G), and
a concentration of all sulfur components in the sample gas (G) and a concentration of sulfur dioxide (SO₂) alone in the sample gas (G) are determined.
<table>
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<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
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<td>X</td>
<td>US 5 531 105 A (COLVIN ALEX D ET AL) 2 July 1996 (1996-07-02) * column 3, line 10 - column 5, line 32; figure 1 *</td>
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<td>WO 02/059566 A (HARRISON DAVID ; ALLEN GEORGE (US); HARVARD COLLEGE (US)) 1 August 2002 (2002-08-01) * page 5, line 3 - page 18, line 4; figure 1 *</td>
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<td>US 5 152 963 A (WREYFORD DONALD M) 6 October 1992 (1992-10-06) * column 2, line 24 - column 6, line 11; figure 1 *</td>
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<td>A</td>
<td>JP 01 239499 A (BABCOCK HITACHI KK) 25 September 1989 (1989-09-25) * abstract; figures 1-3 *</td>
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<td>A</td>
<td>US 3 871 831 A (ANDRAL GUILLAUME ET AL) 18 March 1975 (1975-03-18) * column 1, line 38 - column 2, line 23; figure 1 *</td>
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The present search report has been drawn up for all claims

Place of search Date of completion of the search Examiner
Munich 26 March 2010 Duijs, Eric

CATEGORY OF CITED DOCUMENTS
X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
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26-03-2010

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