PATENT SPECIFICATION

(11) 1 566 436

1 566 436

(21) Application No. 43745/76 (22) Filed 21 Oct. 1976
(31) Convention Application No. 2553565
(32) Filed 28 Nov. 1975 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 30 April 1980
(51) INT CL³ G01N 21/31
(52) Index at acceptance
G1A A4 A6 CD D10 G10 G17 G7 P16 P17 P6 P9 R6 R7 S7 T1 T20

(19)

(54) A DEVICE FOR DETERMINING THE CONCENTRATION OF NITRIC OXIDE IN A GAS MIXTURE

(71) We, HARTMANN & BRAUN AKTIENGESELLSCHAFT of Grafstrasse 97, 6000 Frankfurt/Main, Federal Republic of Germany, a German body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a device for determining the concentration of nitric oxide in a gas mixture by supplying radiation along two paths, one of which contains a vessel for the gas mixture and processing the signals from detection at the end of the paths.

If it is intended to measure small concentrations of the nitric oxide with such a device (German Offenlegungsschrift No. 24 07 133) approximately according to a radiation absorption A=0.1 in the absorption vessel then the equation:

$$\frac{I_M}{I_V} = \text{Const} \cdot (1-A) \qquad (1)$$

is found which reproduces the relationship between the measurement signal I_M, the reference signal I_V and the absorption A, and this may be modified as follows:

$$\alpha(p, T, t) \cdot \frac{I_M}{I_V} = \text{Const} \cdot (1-A) \qquad (2)$$

wherein p is the pressure in a discharge lamp acting as a radiation source, T is the environmental temperature and the time t means that temporal drift of the measurement signal, for example by means of ageing phenomena has been brought about. The disturbance variable α is thus typically between 0.95 and 1.05. At a value A=0.1, α would bring about a measurement fault of $\pm 50\%$ in the concentration of nitric oxide within the stated limits. For the case where a discharge lamp is used which is filled with air of the appropriate under-pressure, a change in the pressure in the lamp can be produced, e.g. as a result of the influence of environmental temperature and as a result of the process of slow gas absorption in the lamp. This change in pressure acts on the emission characteristics of the discharge gas lamp, which radiates two components, one component which emanates from nitric oxide (NO) molecules, the condition of which corresponds to a charge temperature of approximately 300 Kelvin and one component corresponding to a charge temperature of approximately 1500 Kelvin. At this component ratio depends on the gas pressure the measurement error depends on this in the first instance.

The filter vessel used in the modulation device and filled with nitric oxide gas also behaves in a similar manner and finally a monochromator or an interference filter provided instead thereof exercises an erroneous influence on the result of measurement as a result of ageing and a certain temperature dependence. The influences stated are assembled in the disturbance factor α.

The invention seeks to reduce or possibly eliminate this influence of the disturbance variable on the result of measurement of the analyzer in the region of small gas concentrations.

According to the invention there is provided a gas detector for detecting the concentration of nitric oxide in a gas mixture comprising a hollow cathode lamp containing air at reduced pressure and driven by low discharge current and emitting resonance radiation of nitric oxide, a nitric oxide filter, beam modulation means for moving the nitric oxide filter alternately into and out of the path of the radiation, a monochromator or interference filter positioned in the radiation path after the nitric oxide filter, a beam splitter positioned after the monochromator or interference filter to divide the radiation path into two paths, a vessel for the gaseous mixture in one of said two paths, a detector at the end of each of said two paths, each detector for receiving two alternating amounts of radiation whose alternation is controlled by the beam modulation means and means for producing quotients from the simultaneous output signals of the detectors and further means for processing these quotients to produce a value related to the concentration of nitric oxide.

In order that the invention and its various other preferred features may be understood more easily, embodiments thereof will now be described, by way of example only, with reference to the drawings, wherein:—

Fig. 1 is a schematic diagram of a first embodiment in accordance with the invention,

Fig. 2 is a schematic diagram of a second embodiment, and

Fig. 3 shows a block diagram of a signal processing device in accordance with the invention.

In Fig. 1 a hollow cathode lamp 1 contains air at reduced pressure and is driven by a low discharge current, whereby the hollow cathode lamp emits radiation in the resonance range of nitric oxide which radiation is modulated by a circulating disc or plate 2, which contains two filter vessels 3 and 4. The filter vessel 3 is filled with nitric oxide and preferably is under a pressure of 1 atmosphere and absorbs a part of the radiation when the vessel enters into the path of rays. On the other hand the radiation is not affected when the vessel 4 filled with air enters the path of the rays. The vessel walls of the filter vessels penetrated by the radiation comprise a material which is transmissive in the spectral range of the radiation. A lens 5 produces a parallel beam of rays of the two components of the rays which are filtered and unfiltered periodically following one another, the components of the rays reach a beam splitter 7 after passing through an interference filter 6. The beam splitter is a semitransmissive mirror with the aid of which radiation is partially deflected into a beam receiver 8. In a conventional manner the non-deflected part of the radiation penetrates an absorption vessel 9 charged with the test gas and then reaches a beam receiver 10. The beam receiver 8, for example a photomultiplier, periodically emits two signals I_{MO} and I_{VO}, the level of which is proportional to the unfiltered radiation and the radiation filtered by the filter vessel. Signals I_M and I_V of the beam receiver 10 are determined from the filtered and unfiltered ray dependent on its absorption in the absorption vessel 9. The signals I_V, I_{VO}, or I_M, I_{MO} occur at the same time respectively. The index M indicates that the signal is brought about by the beam component which is not influenced by the filter vessel of the modulation device (measurement beam), the index V relates to a signal which emanates from the filtered beam (reference beam). The index O indicates that the beams and thus the signals are not influenced by the gas mixture in the absorption vessel 9.

From Equation (2) the following is obtained:

$$\alpha(p, T, t) \cdot \frac{I_{MO}}{I_{VO}} = \text{const.} \qquad (3)$$

From Equations (2) and (3) there follows:

$$\frac{I_{VO}}{I_{MO}} \cdot \frac{I_M}{I_V} = (1-A) \qquad (4)$$

This equation contains only the absorption A of the resonance radiation of nitric oxide as an unknown factor in the measurement vessel in accordance with the component of nitric oxide in the gas mixture to be measured. If from the four signals I_M, I_V, I_{MO} and I_{VO} Equation (4) is formed then a signal which is not influenced by the disturbance variable α is obtained for the variable of A and thus the concentration of nitric oxide according to the relationship:

$$A = \frac{\dfrac{I_V}{I_{VO}} - \dfrac{I_M}{I_{MO}}}{\dfrac{I_V}{I_{VO}}},$$

Fig. 3 shows the general circuit diagram of a signal processing unit for this relationship. The signals I_{MO}, I_{VO} or I_M, I_V, which are emitted by the two radiation receivers 8 and 10 and amplified by the amplifiers 11 and 12, are supplied to a divider 13. The latter forms the two quotient values corresponding to

$$\frac{I_M}{I_{MO}} \quad \text{and} \quad \frac{I_V}{I_{VO}}$$

which follow periodically one after the other and reach a switching device 14. The switching device causes the two values to be routed on separate channels with the aid of a control signal on the line 15. The synchronous control signal required for this is supplied, in known manner, by a photocell 16 influenced by a lamp 17 the radiation of which falls through a slit 18 in the diaphragm 2 on to the photocell (Fig. 1). In a differential amplifier 19 and a further divider 20 the ratio

$$\frac{\dfrac{I_V}{I_{VO}} - \dfrac{I_M}{I_{MO}}}{\dfrac{I_V}{I_{VO}}}$$

is finally formed. A low-pass filter 22 for smoothing the signal is connected at the input side of the indicating device 21 for A and thus for the concentration of nitric oxide.

Equation (4) may also be converted in a different manner so that it is possible to provide variously constructed signal processing units for determining the measurement variable.

In the device of Fig. 2 an absorption vessel 23 is irradiated twice by using a reflector 24. A partially transmissive mirror 25 directs a comparison beam into one beam receiver and a reflected measurement beam into the beam receiver 26 which periodically emits signals corresponding to I_M and I_V. Otherwise the arrangement corresponds to that of Fig. 1. Instead of a partially transmissive mirror for dividing up the beam a quartz plate may also be used or a mirror having a central opening.

WHAT WE CLAIM IS:—

1. A gas detector for detecting the concentration of nitric oxide in a gas mixture comprising a hollow cathode lamp containing air at reduced pressure and driven by low discharge current and emitting resonance radiation of nitric oxide, a nitric oxide filter, beam modulation means for moving the nitric oxide filter alternately into and out of the path of the radiation, a monochromator or interference filter positioned in the radiation path after the nitric oxide filter, a beam splitter positioned after the monochromator or interference filter to divide the radiation path into two paths, a vessel for the gaseous mixture in one of said two paths, a detector at the end of each of said two paths, each detector for receiving two alternating amounts of radiation whose alternation is controlled by the beam modulation means and means for producing quotients from the simultaneous output signals of the detectors and further means for processing these quotients to produce a value related to the concentration of nitric oxide.

2. A device as claimed in claim 1, wherein the beam splitter is a partially transmissive mirror.

3. A device as claimed in claim 1, wherein the beam splitter is a quartz plate.

4. A device as claimed in claim 1, wherein the beam splitter is a mirror having a small central opening.

5. A device as claimed in any one of claims 1 to 5, wherein a reflector is provided for reflecting the radiation of said one of said two paths through the gaseous mixture vessel for a second time.

6. A gas concentration detector substantially as described herein with reference to the drawings.

For the Applicants:
J. F. WILLIAMS & CO.,
Chartered Patent Agents,
34 Tavistock Street,
London, WC2E 7PB.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1566436 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

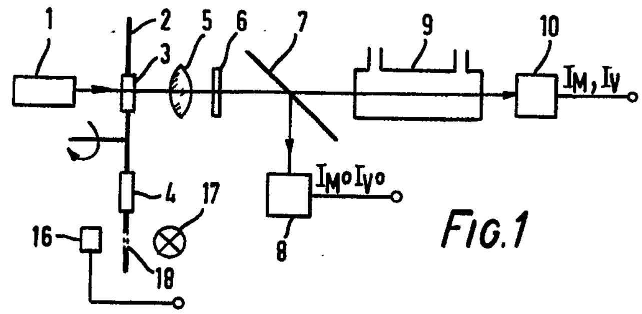

FIG.1

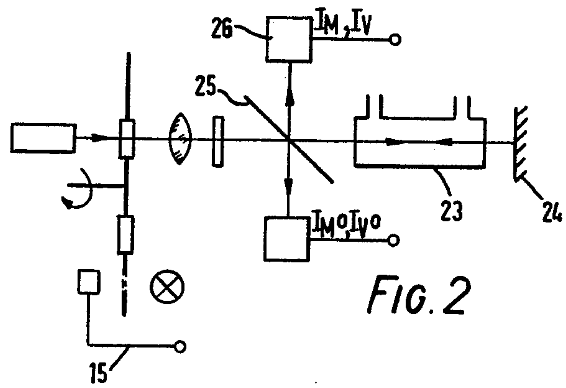

FIG.2

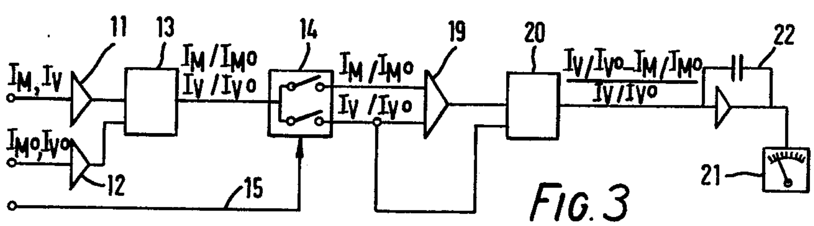

FIG.3