A CALIBRATION DEVICE FOR LONG-PATH SENSORS OF ATMOSPHERIC POLLUTANTS
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A CALIBRATION DEVICE FOR LONG-PATH SENSORS OF
ATMOSPHERIC POLLUTANTS

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ABSTRACT

The calibration of long-path optical sensors of atmospheric pollutants like the Barringer correlation spectrometer is obtained by a device in which the optical pathlength is varied. By using the device here described the calibration procedure requires about 6 min. for the full length expansion of the cell equivalent to concentration-pathlength variation of 1:250.

The device is simple and can be installed on an optical bench i.e. for simulation of polluted atmosphere.
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I. THE NEED OF A CALIBRATION DEVICE

Within the framework of a research activity aiming at the application of optical methods to remote sensing of air pollution, some difficulties have been experienced in calibrating instruments based on resonance absorption, and suitable for air quality measurements over a long pathlength. Instruments for this application are correlation spectrometers (i.e., Barringer (x) Cospec™) which uses a modulated Xe lamp for average concentration measurements of $\text{SO}_2$ at around 310 nm and of $\text{NO}_2$ at around 440 nm, and tunable laser analysers which use specific absorption of infrared light emitted by a diode laser or by other tunable laser device(1).

The classical ways of calibrating these absorption analysers are: 1) by inserting two optical standards and extrapolating a linear relationship to a zero level or 2) by introducing some mixtures of gases at different concentrations in a cell having a fixed length. Practically for a correct calibration following method 2), some difficulties are experienced, for example  a) it is necessary to prepare and to store large volumes of gas mixtures at very low concentration,  b) the analysis of gas mixtures at a concentration of ppm or lower requires large volumes of gases or some sophisticated techniques and  c) the wall effect in the cell and in the container may modify the mixture composition.

For these reasons we studied a device which by varying the length could permit a calibration by using a gas mixture only.
II. THE VARIABLE PATHLENGTH CELL

The device we realised and its schematic are shown in fig. 1 and 2 respectively. Essentially, it consists of two cylindrical teflon bellows cells \( (C_1, C_2) \), having the left head fixed on the frame holder of the device and the right one moving on three bars; the cells are connected by silicone tubes in order to have a constant pressure. The cells are mounted one upon the other for use on an optical bench. A motor \( (M) \) operated by a button on the front of the holder moves by means of a driving cam \( (B) \) one of the right heads towards the fixed one, and the other in the opposite direction. The PVC heads hold the optical windows \( (W) \); the left heads hold the optical windows by a teflon cylinder some cm in length placed inside the bellows to allow a zero thickness in the cell when compressed. In one connecting tube, an inlet valve \( (I) \) for gas filling and a teflon fan \( (F) \) operated by a motor are inserted. To wash the gas circuit, an exit valve \( (V) \) is inserted in one left head. The mode of operation is quite simple: the circuit is flushed with the gas mixture to be used for several minutes; once \( (I) \) and \( (V) \) have been closed by simply pushing the buttons for \( (M) \) and \( (F) \) the cell length can be varied from about zero to the maximum value of \( b \) possible. The pathlength \( b \) of one cell is given by a indicator on a meter scale on the front of the frame holder; in a more sophisticated way, the \( b \) values can be transferred to a recorder \( (R) \) via a potentiometer connected to \( (B) \). A two-pen recorder can display simultaneously the gas signal and \( b \) values. In our device the maximum pathlength is 50 cm with a minimum of 0.2 corresponding to a concentration path length \( (c \cdot b) \) range of 1 : 250. By introducing i.e. the commercial gas mixture \( \text{SO}_2/\text{N}_2 \) at 100 ppm (in vol.) we can get \( c \cdot b \) values from 50 ppm-m down to 0.2 ppm-m. These data are equivalent over a 1000 m optical path to concentrations from 50 to 0.2 ppb. The concentration range 1 : 250 fully covers the concentration range of most of the pollutants.
in the atmosphere.
The device operates at atmospheric pressure but a somewhat lower pressure can be used. It is quite simple, easy to realize and can be installed on an optical bench, i.e. for simulation of polluted atmosphere.

III. DETAILED DESCRIPTION (fig. 2)

**Cells** \((C_1, C_2)\) They consist of teflon bellows \((fig. 3)\), 600 mm length, external diameter 120 mm, internal diameter 80 mm, with 45 coils. The bellows are made by direct melting. The minimum length one can obtain is 120 mm. At one side of the cell a teflon cylinder 113 mm length, 78 mm diameter is inserted. At the internal end of the teflon cylinder the optical windows \((w)\) are welded by Araldite type Ay 101. For operation in the ultraviolet/visible spectral region, which is the case of Barringer Cospec analyser, Tetrasil A discs 78 mm diameter, 6 mm thickness have been used. In the infrared region KRS-5 windows could be used.

**Fan** \((F)\) It is a mixing teflon fan moved by an electric motor Crouset type 82160, 3000 rpm. The gas tightness is assured by Viton type O-rings resistant to most of corrosive gases.

**Connecting tubes** \((T)\) These are silicone tubes HW/55 type, 14 mm external diameter.

**Motor** \((M)\) It is a Isotermic Swiss speed reducer with a reduction ratio 405 : 1 with 5,9 rpm. The motor moves the screw cams \((B)\) by gears.

**Bars** \((B)\) Both the screw cams and the fixed bars are in stainless steel. The screw cams move on ball bearings and their position is regulated by two microswitches.

**Potentiometer** \((P)\) It is a Helipot type potentiometer with an accuracy of 0.25% and a resistance of 0.5 KΩ.

**Recorder** \((R)\) It is a two pen recorder 10 mV full scale we use a Philips type 8221 PM recorder.
Valves (V and three ways valve Y) are teflon or glass valves. The device holder is in aluminium AG-3: the front panel has two buttons for (M) and (F) and a meter for the direct reading of the lower cell length. The bellows are moved by the motor (M) through two gears; when one cell reaches the maximum optical length of 500 mm, the other reaches the minimum optical length of 2 mm (obviously these distances refer to the internal walls of the windows). The speed of pathlength variation is 82 mm/min., the full expansion being obtained in about 6 minutes. The length of the lower cell can be read (a) directly on the meter scale or (b) on the recorder simultaneously with the gas signal. So one can directly verify the relationship between pathlength and absorption.

IV. MODE OF OPERATION

The mode of operation of this device is quite simple. First the flushing of the system is obtained in the following manner; the valve (I) is connected to a gas supply and (V) is opened. The gas circulates alternatively via (F) and by (C₁) and (C₂), and then on closing (I) and (V) the fan (F) is started for some minutes, after which the gas is removed by (V). This operation is repeated several times until a stable instrumental response is obtained. Once filled the cells and closed (I) and (V), the variation of the pathlength is obtained by pushing the button for (M) on the front panel. In about 6 minutes the pathlength varies from 2 to 500 mm continuously and the length b is recorded together with the gas signal.
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We are indebted to Mr. G. Giovanelli and G. Cesari, Istituto di Fisica dell'Atmosfera del C.N.R. Bologna for the helpful discussions in the realisation of the device.
Fig. 1 - The calibration device
Fig. 2 - Schematic

- C12 Gas cells
- M Motors
- F Fan
- I Inlet valve
- W Optical windows
- V Vacuum connection
- B Bars
- TB Teflon bellows
- R Recorder
- T Connecting tubes
- P Potentiometer

- B Bars
- F1 F2 Gas volume
- W Optical windows
- V Vacuum connection
- B Teflon bellows
- R Recorder
- T Connecting tubes
- P Potentiometer
Fig. 3 - A teflon bellow
Fig. 4
SO$_2$ CALIBRATION

Cell filled with 1000 ppm SO$_2$ in N$_2$
Gaspec III B (Barringer)
Passive mode - AGC = 5.4 V; T.C. = 4 sec
109 mV full scale recorder
Chart speed 1 inch/min.
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