

CALIBRATION OF A RAMAN-LIDAR GAS ANALYZER OF ATMOSPHERIC EMISSIONS FROM PLANT STACKS USING A REMOTE GAS CHAMBER

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We discuss calibration tests of our mobile Raman lidar intended for remote monitoring of atmospheric emissions from plant stacks. The calibration experiments have been conducted to validate its capability of remotely detecting, at the stack mouth, the most common gaseous pollutants like CO, NO, NO₂, and SO₂ using a specially designed gas chamber five meters long and 30 cm in diameter that can alternatively be filled with standard mixtures of the above contaminating species with pure nitrogen. The results obtained in these experiments well demonstrate the best features of the Raman-lidar technique in application to gas concentration measurements and this is illustrated with a perfectly linear concentration behavior of the Raman-lidar return from SO₂ molecules in the concentration range of the latter from 0.05 to 5 % by volume. At the same time the experiments have clearly shown that such instrumental noises as long-lived broad-band luminescence of the chamber windows can impose a serious limitation on the possibility of certifying lidars as regards the minimum detectable concentration, since just this luminescence noise determines the signal-to-noise ratio at low concentration of a gas specie. In addition to this instrumental limitation there can occur certain troubles due to an unavoidable broad-band luminescence of a gas specie, like for example NO₂, when using visible laser radiation to excite Raman effect in a gas mixture under study.

1. INTRODUCTION

Capabilities of Raman lidars to achieve the task of detecting contaminating gaseous species in atmospheric emissions from plant stacks and measuring their number densities have been first demonstrated more than twenty years ago.¹ Moreover, in our recent publications^{2,3} dealing with this problem we have shown that the Raman-lidar approach to monitoring of such emissions enables, in addition, obtaining information on the emission gross yields by simultaneously estimating the emission jet outflow velocity from these same lidar returns though under certain assumptions on the mechanism of the gas mixture ascent inside the stack.

However, for a Raman lidar to be used as a control instrument in an environmental protection service it must be certified. Unfortunately, we couldn't find any publications on this problem in the literature so far. Recently we have started a research work aimed at the development of a certification technique and a facility enabling calibration tests of our mobile Raman lidar.⁴ This work is being done in cooperation with the

Regional Environmental Protection Agency of Khabarovsk region and Scientific and Production Association "Dal'standart" in Khabarovsk.

At the present stage of research under this project we have managed to demonstrate the feasibility of the calibration using a remote gas chamber, that can alternatively be filled with the mixtures of contaminating gases of interest with pure nitrogen. At the same time, the first experimental results have revealed certain technical problems on providing spectral purity of the Raman-lidar returns.

Among the effects interfering the Raman-lidar returns from gases, in this particular experiment, we would separate out the luminescence of the entrance and exit windows of the gas chamber and the luminescence of NO₂ and NO molecules. We distinguish between them because of an obvious reason that the luminescence light coming from windows can be reduced by a proper choice of the window material as well as by increasing the length of the chamber to provide lower level of the luminescence signal from a volume in the middle of the chamber (due to the exponential decay of luminescence in time) and by

some other geometric and optical measures while the luminescence noise coming from a mixture component that may absorb sounding radiation is unavoidable. In order to reduce the level of this spectrally broad noise one should use a much more sophisticated instrumental approach to isolation of the informative Raman-lidar returns from contaminating trace species than it would seem from the first sight. This is just the situation we normally face when trying to monitor the most common gaseous pollutants like CO, NO, NO₂, and SO₂ (in a mixture) using a Raman lidar operating in the visible region, since both NO and NO₂ have broad absorption bands in this region.⁵

2. EXPERIMENTAL SET UP

The optical arrangement of the calibration experiments is depicted in Fig. 1. In this figure is also set out the block-diagram of the gas chamber used.

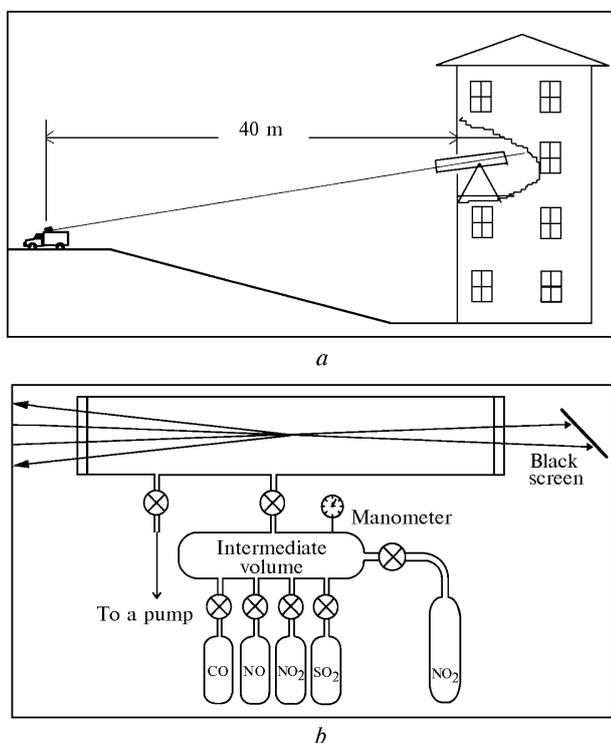


FIG. 1. Optical arrangement of measurements (a) and block-diagram of the chamber (b).

As is seen from this figure the sounding laser beam is focused on a middle region of the gas chamber through its entrance window. Then the beam leaves the chamber through the exit window and impinges a black screen covered with camphor soot that completely absorbs visible light without a detectable re-emission. Radiation scattered backward by molecules due to the Raman effect enters the receiving optical antenna of the Raman lidar. Optical

arrangement of the lidar installed inside an automobile van is shown in Fig. 2.

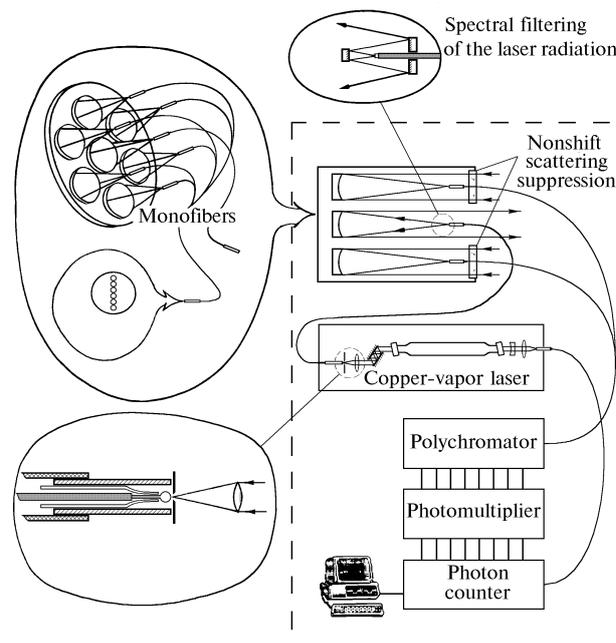


FIG. 2. Optical arrangement of the mobile Raman lidar.

As is seen from this figure the radiation backscattered from the gas chamber is first optically filtered at the optical antenna entrance to suppress the spectral line of unshifted light scattering and then it is entered to a polychromator. The lidar transmitting and receiving antenna is a matrix of seven identical parabolic mirrors the central element of which is used as a beam collimator directing the sounding beam towards a target while six other mirrors collect the radiation scattered backward from it. Sounding radiation is transported from the laser to the transmitting mirror through an optical monofiber of fused silica. Similarly six monofibers are used to transport radiation collected by each receiving mirror of the matrix to the polychromator. The six receiving monofibers are collected in a bundle to form the entrance slit of the spectrometer, as shown in the figure. Use of monofibers as optical connectors between different functional blocks of the lidar provides a very high stability of optical alignment of the lidar as a whole, and moreover, this well suits the requirements to a fieldable version of the lidar. For example, in Fig. 3 is set out the scheme of how our Raman lidar is mounted in an automobile van.

It is well seen from this figure that during the operation only the transceiver optics of the lidar is in open air while other functional blocks are inside the van. The main characteristics of the Raman lidar are given below in the table of specifications.

TABLE I. Specifications of the Raman lidar

Transmitter: (Copper-vapor laser connected via a monofiber with the central mirror of the transmitter-receiver matrix)

Operating wavelength, nm	510.6
Mean output power, W	6
Pulse repetition frequency, kHz	7
Pulse width, ns	10
Angular beam width, mrad	0.5

Receiver: (six outer mirrors of the matrix connected via monofibers with the lidar polychromator)

Diameter of individual mirror, m	0.15
Focal length, m	0.4
Width of the spectral intervals isolated at the exit of the polychromator, nm	0.6

Data acquisition system: (IBM PC – compatible eight-channel photon counter)

Number of channels	8
Number of time gates per channel	1024
Width of a time gate, ns	10

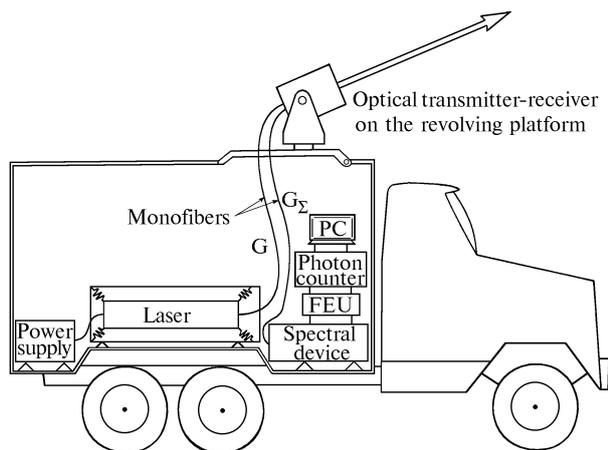


FIG. 3. Block-diagram of the mobile Raman lidar.

3. BACKGROUND AND EXPERIMENTAL RESULTS

Raman-lidar technique for detecting molecules of gaseous air pollution is known to provide a direct measure of their number densities by ratioing Raman-lidar returns from trace gases to simultaneously recorded Raman-lidar return from molecular nitrogen. The latter signal is thus used as an internal standard since the nitrogen concentration may be assumed known or it can readily be estimated from the return signal itself following, for example, the algorithm described in Ref. 3. The ratio of Raman-lidar returns, R , recorded from one and the same scattering volume is normally written as follows:

$$R = \frac{N^{SO_2}}{N^{N_2}} = \frac{\sigma^{SO_2}}{\sigma^{N_2}} \frac{\tau_{SO_2}}{\tau_{N_2}} \frac{q_{SO_2}}{q_{N_2}} \frac{n_{SO_2}}{n_{N_2}}, \quad (1)$$

where N^i is the number of photocounts in the corresponding channel, σ^i is the differential cross-section of Raman backscatter by i th molecular species, τ_i is the end-to-end efficiency of the corresponding spectral channel of the lidar due to optical losses, q_i is the quantum efficiency of the i th photomultiplier, n_i is the number density of a molecular species.

In our calibration experiments we first evacuated the gas chamber and then filled it with a standard gas mixture to be studied up to atmospheric pressure. In the standard mixtures used the concentration of a minor gas was about 5% by volume. Then the mixture was diluted with pure nitrogen step by step. Normally, ten five-minute measurements have been carried out at each concentration of a contaminating gas. Time behavior of the Raman-lidar responses in the spectral channels corresponding to Raman lines of the gases studied, normalized by that from nitrogen, is shown in Fig. 4a for the case when the chamber was filled with the $SO_2 + N_2$ mixture. Figure 4b depicts the above ratio of the SO_2 and N_2 lidar returns, recorded from the scattering volume inside the chamber, as a function of SO_2 concentration measured independently.

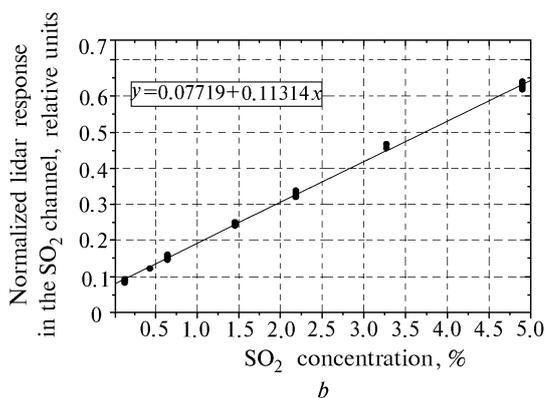
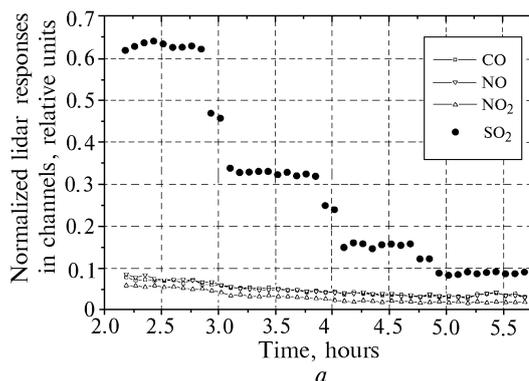


FIG. 4. Normalized lidar responses as functions of time (a) and SO_2 concentration (b).

As is well seen from Fig. 4a time behavior of the normalized lidar response from SO_2 quite accurately follows the step-wise dilution of the gas mixture with pure nitrogen. As a result, the normalized response

from SO_2 , as a function of its concentration, is very well approximated by a straight line. Shown in this same figure are lidar responses, also normalized by return signal from N_2 , simultaneously recorded in the spectral channels of other species. Low values of these ratios as well as only slight variation in time (primarily due to a slight increase in the nitrogen concentration) clearly demonstrate spectral independence of all channels in this case.

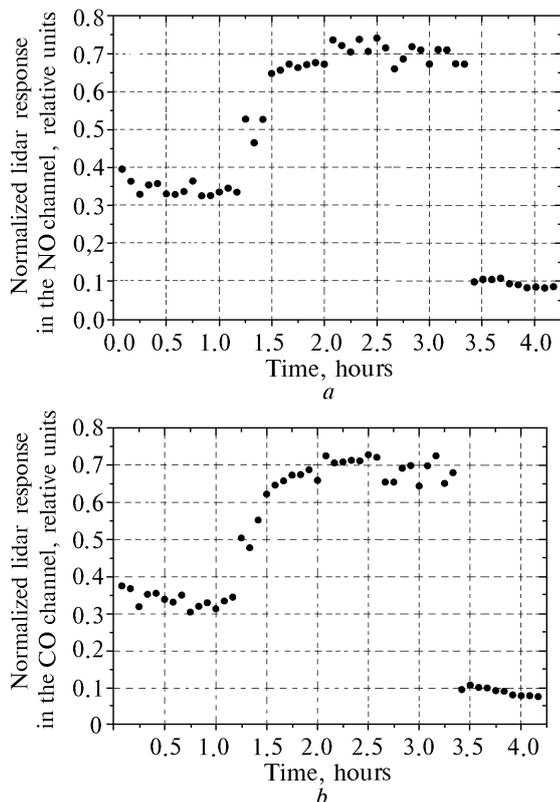


FIG. 5. Normalized lidar responses in the spectral channels of NO (a) and CO (b) as functions of time.

However, the situation is quite different in the case with NO and NO_2 gases because of the long-lived and broad-band luminescence excited by the green line of the copper-vapor laser radiation used. In this case the responses in all spectral channels strongly depend on the concentration of these molecules in the mixture under study. Just to illustrate this fact we present below, in Fig. 5, time behaviors of the normalized lidar responses in the spectral channels of NO and CO Raman bands simultaneously recorded from the volume inside the chamber when filling it with NO + N_2 mixture up to a pressure about tens of Torr.

It is well seen from this figure that simultaneously with the increase of signal in the NO channel similarly increases the signal in the CO channel. It should be noted, for certainty, that the level of luminescence in both channels is high at low pressure when the luminescence is not quenched. The abrupt fall off of the signals at about 3 hours is due to efficient quenching by nitrogen molecules that were added to make the total pressure equal to 1 atm.

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