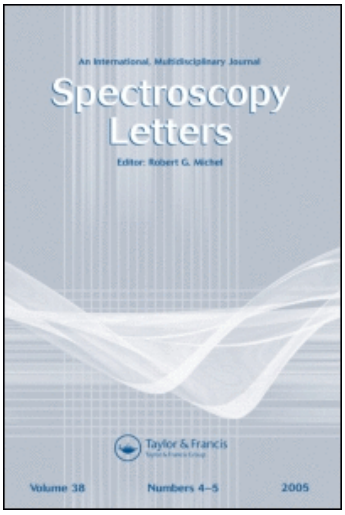

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MOLECULAR AIR POLLUTION MONITORING BY PULSED CO_2 LASER-BASED LONG-PATH TECHNIQUE

KEY WORDS: atmospheric pollution monitoring, differential absorption technique, double-ended lidar, pyroelectric detector

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Abstract

Double-ended experimental arrangement using a small tunable TEA CO_2 laser and a retroreflector was employed for differential absorption measurements of ethylene, freon 12 and ammonia concentrations in the atmospheric air in the distant sample chamber. Telescope collected return radiation was detected with a pyroelectric detector. Good agreement between remotely and in-situ measured concentrations was obtained. The system sensitivity to investigated gases was found to be of the order of several ppb-kilometers.

INTRODUCTION

The differential absorption method is considered as being one of the most powerfull lidar (optical radar) techniques for remote measurement of atmospheric pollution (see e.g. Ref. (1)-(3)). The method is spectroscopic in its nature and it relies on the use of selected laser wavelengths in coincidence with absorption features of gaseous atmospheric pollutants.

Existing practical systems for differential absorption air pollution measurements can be divided in three groups which make use of cooperative reflectors, solid scattering surfaces or atmospheric aerosols to provide a return signal (see e.g. Refs. (4)-(7)).

Systems belonging to the first group are double-ended and based on the use of cooperative reflectors (retroreflectors). They are capable of measuring the average concentration of air pollutant between the laser transmitter/receiver and a remotely located retroreflector. These systems have the advantage of using a low-powered laser and a small receiving telescope, or a less sensitive photodetector. Systems from the second group use back-scattering from topographic targets to provide the return signal and also measure the average concentration between the transmitter/receiver and an arbitrary solid scattering surface. Lidar systems which use backscattering from naturally occuring aerosols in the atmosphere belong to the third group. Such systems are trully single-ended and are capable of range resolved measurements. Of all three groups they require the most powerfull lasers, the largest receiving telescopes and the most sensitive photodetectors.

The aim of this paper is to report results of differential absorption measurements of small concentrations of ethylene, freon 12 and ammonia in atmospheric air. The experimental setup is based on the use of a small tunable pulsed CO_2 laser. Pyroelectric detector is employed to detect return infrared radiation.

THEORY

Differential absorption technique uses at least two wavelengths. One is coincident with the absorption maximum of the pollutant gas and hence it is strongly absorbed (resonant wavelength), while the other is outside the absorption maximum (non-resonant wavelength). The non-resonant wavelength is used essentially to calibrate the reflectivity of the

target, atmospheric propagation losses, and characteristics of the receiver system. It should be pointed out that the emitted laser wavelengths must be closely spaced if contributions other than from the species of interest are to be eliminated. The difference between the received signals at resonant and non-resonant wavelength is a measure of the degree of absorption by the gaseous pollutant and it is used to determine the concentration of the absorbing species present in the atmosphere.

Systems using retroreflectors or topographic scatterers can be used only to perform path-integrated differential absorption measurements. Starting from the well known absorption law, the following expression containing integrated concentrations of all the absorbing species along the laser beam path can be written

$$\ln \frac{I(\lambda_N)}{I(\lambda_R)} = 2 \sum_{i=1}^{k} \{[\sigma_i(\lambda_R)-\sigma_i(\lambda_N)] \int_0^{\ell_i} N_i(r)dr\} \qquad (1)$$

where $I(\lambda_R)$, $I(\lambda_N)$ are received radiation intensities at resonant (λ_R) and non-resonant (λ_N) wavelength respectively; $\sigma_i(\lambda_R)$, $\sigma_i(\lambda_N)$ i species absorption cross sections at two wavelengths; $N_i(r)$ i - species number density at distance r from the measuring device; ℓ_i beam pathlength through the medium containing absorbing species i; k number of different absorbing species along the path of the laser beam. In eq. (1) it is assumed that transmitted intensities at two probing wavelengths are equal.

In atmospheric pollution measurements we are concerned with evaluation of the concentration of specific pollutant and contributions of other constituents of the atmosphere to the total absorption are treated as an interference. Assuming that concentrations of all the absorbing species i are homogeneously distributed with average concentrations $\bar{N}$ the concentration of the specific pollutant $\bar{N}_p$ can be easily derived from eq. (1)

$$\bar{N}_p = \frac{1}{2L[\sigma_p(\lambda_R)-\sigma_p(\lambda_N)]} \left[\ln \frac{I(\lambda_N)}{I(\lambda_R)} - K\right] \quad , \qquad (2)$$

where L is the distance from the transmitter/receiver to the reflector. The differential absorption correction term K due to interferent absorbing species present in the atmosphere is given by the following expression

$$K = 2 \sum_{i=1}^{k-1} [\sigma_i(\lambda_R) - \sigma_i(\lambda_N)] \bar{N}_i L \quad . \tag{3}$$

One should notice that in the sum of eq. (3) terms with negative sign can also appear, reflecting the fact that $\sigma_i(\lambda_N)$ can be greater tran $\sigma_i(\lambda_R)$.

EXPERIMENTAL APPARATUS AND PROCEDURE

A block diagram of our long-path atmospheric monitoring apparatus is shown in Fig. 1. A small-scale grating tuned TEA CO_2 laser was used as the source of radiation. A variable aperture was incorporated in the laser resonator cavity and it was used for transverse-mode selection. The laser beam was transmitted coaxially to the receiving telescope and directed to a sample chamber located 1.2 km from the transmitter/receiver facility. The length of the cylindrically shaped sample chamber along its optical axis was 1.15 m and its diameter was 0.85 m. The front aperture of the chamber was closed with 0.05 mm thick polyethylene window mounted at angle od 15^o from the plane of retroreflector to minimize surface reflections. The back wall of the sample chamber was entirely covered with a large number of 4 mm diameter cube corner retroreflectors. For this purpose back side of commercially produced plastic retroreflectors (used for truck back-lights) was used. In order to achieve high reflectivity at CO_2 laser wavelengths aluminum was vacuum deposited on plastic. Ouick change of gas mixtures in the sample chamber was attained with the aid of an exhaust fan. This fan was also used for mixing the pollutant gas with atmospheric air, so that homogeneous distribution in the chamber was obtained.

Radiation reflected back from the retroreflector was collected by a Newtonian telescope with 20.3 cm (8 inches) aperture. ZnSe lense provided

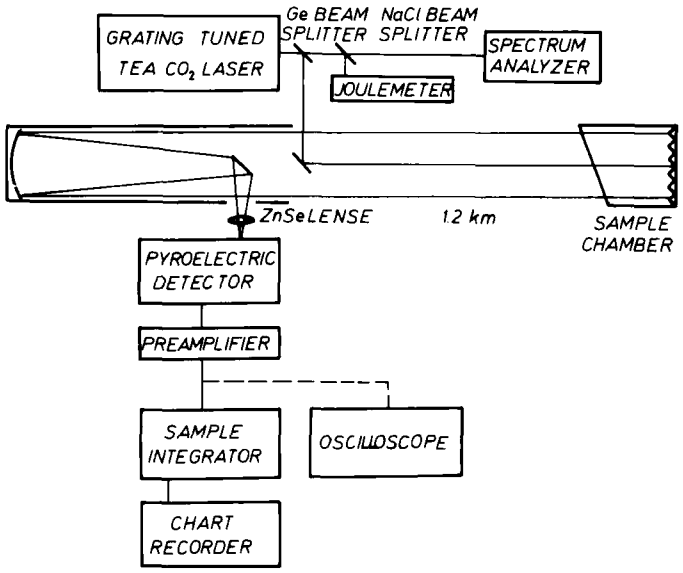

Fig. 1. Block diagram of the laser differential absorption long-path pollution monitoring apparatus.

additional focusing of received radiation onto the lithium-tantalate pyroelectric detector (New England Research Center LTO-B100/OPF-100) with circular sensing element of 1,25 mm diameter.

As depicted in Fig. 1, a fraction of the CO_2 laser beam was directed towards a joulemeter and a spectrum analyzer. The receiver electronics consisted of pyroelectric detector preamplifier, sample integrator and a chart recorder with a temporary use of an oscilloscope.Parameters of the whole system are given in Table I.

At least 140 return pulses at each wavelength were averaged using sample integrator and displayed at chart recorder. It took 2-3 minutes to complete measurements at one wavelength. The laser output energy at different emitting wavelengths was held constant. Special care was taken to make sure that the sequentially transmitted laser beams at different wavelengths are collinear and of similar cross-section patterns as close as possible to TEM_{00} mode.

Table I. Experimental parameters

CO_2 laser transmitter:	
energy	100-350 mJ/pulse
pulsewidth	100 nS
pulse repetition frequency	1.2 Hz
beam divergence	3 mrad (TEM_{00})
receiver:	
telescope diameter	20.3 cm
pyroelectric detector $D^*_{BB}(1000,10,1)$ (low frequency value)	$1.1 \cdot 10^8$ cm $Hz^{1/2}W^{-1}$

Calibrated gas syringe was used to prepare samples of polluted air. Known volume of the gas was injected in the sample chamber, so that pollutant concentrations can be directly calculated and compared with remote measurements.

EXPERIMENTAL RESULTS

Long-path pollution monitoring apparatus described in the previous section was used to measure the concentration of ethylene (C_2H_4), freon 12 (CCl_2F_2) and ammonia (NH_3) in atmospheric air of the remotely located sample chamber. On the basis of known absorption coefficients of these gases at CO_2 laser wavelengths[8] resonant and non-resonant CO_2 laser lines were chosen (Table II). The ratio of non-resonant to resonant line received intensities $I(\lambda_N)/I(\lambda_R)$(eq. (2)) was determined from average values displayed on the chart recorder.

Table II. CO_2 laser wavelengths used for pollutant monitoring

Pollutant gas	CO_2 laser line (00^01-10^00) band	Wavelength [μm]	Absorption coefficient [$atm^{-1}cm^{-1}$]
ethylene (C_2H_4)	resonant P(14	10.532	32.17
	non-resonant P(22)	10.611	1.42
freon 12(CCl_2F_2)	resonant P(34)	10.741	44.68
	non-resonant P(22)	10.611	0.60
ammonia (NH_3)	resonant R(8)	10.334	25.83
	non-resonant R(12)	10.303	0.07

At CO_2 laser wavelengths most of the interferences come from the absorption due to water vapor and carbon dioxide normally present in the atmosphere. For our experimental apparatus additional source of interference comes from the of the sample chamber polyethylene window. Therefore interference correction term (eq. (3)) has the following form

$$K = K_H + K_C + K_W, \tag{4}$$

where K_H is the correction due to water vapor, K_C due to carbon dioxide and K_W due to sample chamber window. Water vapor correction term was estimated using absorption coefficients measured by Shumate et al.[9], and by taking into account the relative humidity (40%-50%) and temperature (23^oC - 27^oC) of the air on the days of measurements. Correction due to atmospheric carbon dioxide was calculated from the CO_2 line strengths data of Young and Chapman[10] and Devir and Oppenheim[11]. For this calculation the assumed amount of carbon dioxide in the atmospheric air was 330 ppm[1],[4]. The polyethylene window differential absorption correction term was evaluated from the data obtained with high resolution infrared spectrophotometer. For all CO_2 laser wavelengths used and in all experimental conditions, window

correction term K_w had a small value, never exceeding 25% of the total correction term. Total interference correction factor K (eqs. (3) and (4)) was calculated for each three pairs of wavelengths (see Table II). The absolute value of the total correction expressed as equivalent ppb-km concentration--pathlength product for particular pollutant was 13.3 ppb-km for ethylene, 7,7 ppb-km for freon 12 and 57.23 ppb-km for ammonia. High value obtained for ammonia is due to relatively strong water vapor interference on R(8) and R(12) lines of $00^0 1\text{-}10^0 0$ CO_2 laser band.

Experimental results of the remote concentration measurements of ethylene, freon 12 and ammonia-polluted air in the sample chamber are shown in Fig. 2. The concentration determined by differential absorption is plotted as a function of the value determined from the injected volume of pollutant gas divided by the sample chamber volume. Solid line in diagrams of Fig. 2 represents hypothetical perfect agreement of remote measured concentrations with syringe injected data. The vertical axis on the right-hand side shows the equivalent concentration-pathlength product in units of ppb-km. Error bars in the diagrams represent uncertainties of measurements induced by the random fluctuations of the return signal, which was not the same for all measured points, since the random fluctuations varied somewhat from one point to another. Sources of these fluctuations were: laser pulse-to-pulse instability, occasional laser arcing, atmospheric turbulence and variations in aerosol scattering. Laser pulse-to-pulse instability was not found to be crucial for the measurements when 140 pulses were integrated. For most of the measurements in Fig. 2 transmitted laser energy was 170 mJ in 100 ns pulses, although 125 mJ was found to be sufficient.

In long-path concentration measurements the system sensitivity is usually defined as the equivalent concentration - pathlength product for which the measured average uncertainty equals concentration. When this definition is applied to our system sensitivities to three investigated gases are found to be 2.6 ppb-km for ethylene, 2.4 ppb-km for freon 12 and 3.1 ppb-km for ammonia.

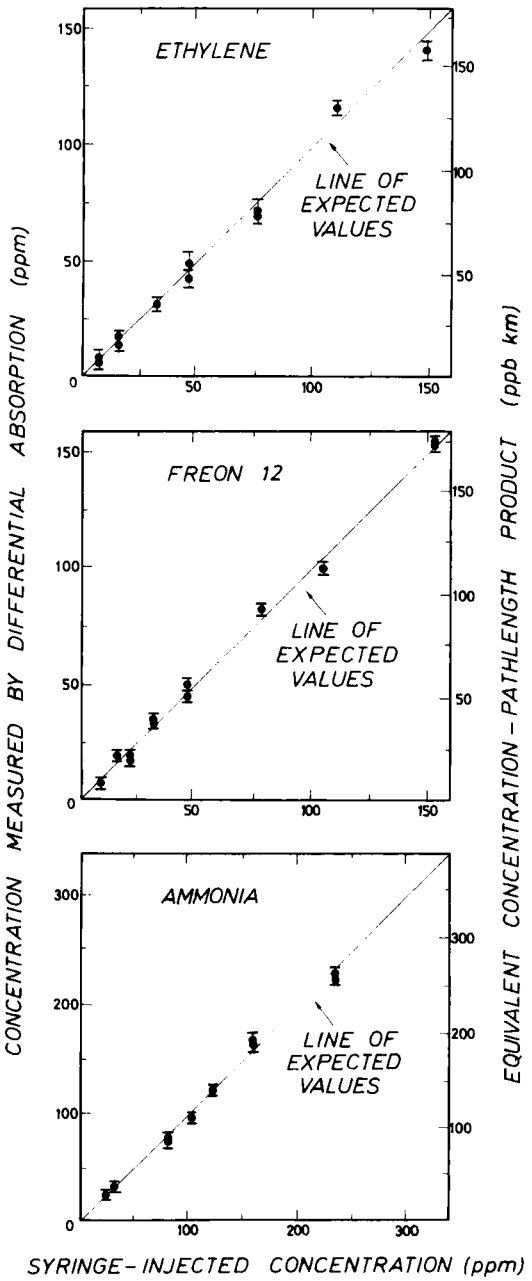

Fig. 2. Results of remote concentration measurements of pollutant gases in the sample chamber at a distance of 1.2 km.

CONCLUSIONS

The investigation reported here explores the applicability of a simple small-scale apparatus for remote air pollution monitoring. The functioning of the apparatus is based on the double-ended long-path differential absorption scheme. A pyroelectric detector was used for the detection of telescope-collected radiation. With this experimental setup concentrations at the level of several ppb-kilometers of ethylene, freon 12 and ammonia can be measured with minimal pulse energies of 125 mJ. General agreement between differential-absorption measured and syringe injected concentrations is indicative of low systematic error.

Here we should amphasize the advantage of long-path pollution monitoring system which uses pyroelectric detector for detection of return infrared radiation. These detectors possess some distinguished features among infrared detectors e.g. ruggedness and reliability, ambient temperature operation and low cost, although their sensitivity is considerably lower than that of some other types. The use of pyroelectric detector and relative simplicity of the whole apparatus, enables the construction of a rugged, compact, moderate-priced air pollution monitor. The double-ended arrangement restricts the use of the apparatus to stationary pollution measurements only, but with several retroreflectors a rather large area could be easily covered with a single transmitter/ receiver unit. This arrangements seems to be appropriate for urban and industrial pollution measurements. Due to its operation around 10 μm, the described system is favorable from the point of view of eye and skin-safety. According to ANSI[12] and British standards (BS 4804)[13] the maximum permissible exposure level for the laser source used in the experiment described here is 10 mJ cm^{-2}. If our apparatus is operated with 125 mJ of transmitted energy (sufficient for 1.2 km distance to the retroreflector as reported here) it becomes safe at all distances greater than 7 m from the transmitter. If the retroreflector is located at somewhat shorter distances, or if larger receiving telescope is used,the

monitoring apparatus could be easily made eye-and skin-safe even immediately in front of the transmitter.

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