

SELECTION OF OPTIMAL SPECTRAL CHANNELS FOR SOLVING THE PROBLEMS OF ABSORPTION GAS ANALYSIS AND REMOTE SENSING. PART II. SEARCH AND RETREIVAL ALGORITHMS

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Algorithms of searching for informative spectral intervals are given in this paper for different absorption gas analysis including optoacoustic, spectrophotometric, and long-path absorption laser techniques. The algorithms are based on calculating information length. These algorithms can be used for making calculations without a computer. Some results of calculations of the information length for the above gas-analysis techniques are presented.

An automated retrieval of spectral channels using an atlas of absorption lines can be performed in the following way. First, the spectral regions are sought for with a rough spectral resolution and then the retrieval among thus selected regions is reiterated, each time with higher spectral resolution till the spectral resolution determined by the width of an interference filter used in the experiment or by the width of the laser radiation spectrum is reached.

Any method of selecting optimal spectral channels calls for relevant algorithms, i.e., rules according to which one or another wavelength for a measurement system with prescribed spectral and energy characteristics are chosen. In the present paper this problem is reduced to calculating some generalized parameter and then to comparing this parameter with a threshold value. It is proposed that the informative distance L to be used as an analyzed parameter. Based on the developed general algorithm¹ we have derived formulas for calculating L in an explicit form for two types of spectral instruments, i.e., spectrophotometric and optoacoustic, as well as for a laser long-path absorption gas analyzer. The results of selecting optical channels are provided.

1. INFORMATIVE REGIONS FOR SPECTROPHOTOMETRIC INSTRUMENTS

A response of a spectrophotometric device to radiation passed through the medium at the wavelength λ is described by the well-known expression

$$I(\nu) = \eta \int_{\Delta\nu} \tilde{g}(\nu, \nu') I_0(\nu') e^{-K(\nu')\rho l} e^{-\tau(\nu')} d\nu', \quad (1)$$

where η is the instrument sensitivity, which is assumed constant within the interval $\Delta\nu$; $\tilde{g}(\nu, \nu')$ is the function of the system response, $I_0(\nu')$ is the radiation intensity at the propagation channel input, $k(\nu')$ is the coefficient of absorption per unit concentration, l is the path length, $\tau(\nu')$ is the optical thickness of other gases and aerosol component. Let us introduce the following designations:

$$g(\nu, \nu') = \frac{\tilde{g}(\nu, \nu') I_0(\nu')}{\int_{\Delta\nu} \tilde{g}(\nu, \nu') I_0(\nu') d\nu'};$$

$$I_0(\nu) = \int_{\Delta\nu} \tilde{g}(\nu, \nu') I_0(\nu') d\nu'.$$

Then relation (1) takes the form

$$I(\nu) = \eta I_0(\nu) \int_{\Delta\nu} g(\nu, \nu') I_0(\nu') e^{-K(\nu')\rho l} e^{-\tau(\nu')} d\nu', \quad (1a)$$

where $\int_{\Delta\nu} g(\nu, \nu') d\nu' = 1$.

The matrix G (see Eq. (10) in Ref. 1) for a single-parameter state (one gas is considered and $m = 1$) at a single wavelength has only one component

$$G(\rho) = \frac{1}{\sigma^2} \left(\frac{\partial F}{\partial \rho} \right)^2 = \frac{I_0^2 \eta^2 l^2}{\sigma^2} \left[\int_{\Delta\nu} g(\nu, \nu') K(\nu') e^{-K(\nu')\rho l} e^{-\tau(\nu')} d\nu' \right]^2,$$

and the information length (according to Eq. (17) from Ref. 1) is determined by the relation (for the interval $\rho \in [\rho_1, \rho_2]$)

$$L = B [T(\rho_1) - T(\rho_2)] = \frac{I(\rho_2)}{\sigma} \left[\frac{T(\rho_1)}{T(\rho_2)} - 1 \right]; \quad (2)$$

$$T(\rho, \tau) = \int_{\Delta\nu} g(\nu, \nu') e^{-K(\nu')\rho l} e^{-\tau(\nu')} d\nu', \quad (3)$$

$$B = I_0 \eta / \sigma.$$

Here T is the transmission function and the value σ is determined by the formula (see Eq. (7) in Ref. 1)

$$\sigma = \sqrt{\sigma_I^2 + \sigma_{I_0}^2 \eta^2 T^2(\rho_1, \tau)}, \quad \rho_1 < \rho_2. \quad (4)$$

Let us assume that in this spectral interval there are absorption bands of several gases and we are going to find a transmission window. To do this, we make use of formula (16) (see Ref. 1) in which ρ_j^{\min} are assumed to be zero

$$L = B \sum_{j=1}^m [T(0, \tau) - T(\rho_j^{\max}, \tau)],$$

where

$$T(\rho_j^{\max}, \tau) = \int_{\Delta\nu} g(\nu, \nu') \exp(-K_f(\nu) \rho_j^{\max} l) \exp[-\tau(\nu')] d\nu, \quad (5)$$

$$\tau(\nu) = \sum_{r \neq j}^{m-1} K_r(\nu) \rho_r^{\text{bg}} l + \tau_a(\nu).$$

Here ρ_r^{bg} is the background concentration of the r th gas, τ_a is the aerosol component of the atmospheric optical thickness, and m is the number of gases. For the ρ_j^{\max} values one can use any values, e.g., $\rho_j^{\max} = \rho_r^{\text{bg}}$. The value σ entering into B is determined by the formula

$$\sigma = \sqrt{\sigma_I^2 + \sigma_{I_0}^2 \eta^2 T^2(0, \tau)}. \quad (6)$$

To simplify calculations the values σ in Eqs. (4) and (6) are assumed to be $T^2 = 1$. This makes the requirements on selection of informative spectral regions more strict. In addition, it is advisable to keep in mind that the constant of the system calibration η is found with some error σ_η . Stringent account of this fact in the present problem leads to unjustified complication of the algorithm. Therefore we make use of an approximated account for the error in assigning η . In Eqs. (4) and (6) there will appear one more term $\sigma_\eta^2 I_0^2 T^2$ and when $T^2 = 1$ we obtain

$$\sigma = \sqrt{\sigma_I^2 + \sigma_{I_0}^2 \eta^2 + \sigma_\eta^2 I_0^2} \leq \sqrt{(\delta_I^2 + \delta_{I_0}^2 + \delta_\eta^2) (\eta I_0)^2}, \quad (6a)$$

where δI , δI_0 , and δ_η are relative errors of I , I_0 , and η measurements. The value $B = I_0 \eta / \sqrt{\sigma_I^2 + \sigma_{I_0}^2 \eta^2 + \sigma_\eta^2 I_0^2}$ characterizes the measuring instrument and represents the signal-to-noise ratio of the measuring system as a whole.

The problems of sounding call for selection of regions with a minimum information length L (ideally, $L \sim 0$), while the problems of gas analysis call for selecting intervals with a maximum L for a given range of gas concentrations $\rho \in [\rho_1, \rho_2]$, in this case $L \geq L_0$, where L_0 is the threshold value equal to 3.3.

Thus the problem on determining informative spectral regions for photometric instruments with response (1) is reduced to calculating transmission functions (3) and (5).

Let us briefly overview the methods for calculating the transmission functions. In accordance with the spectral interval width we consider a broadband, narrow-band, and a monochromatic transmission function.

Broadband transmission functions. The broadband transmission functions are transmission functions for spectral resolution $\Delta\nu \gg \gamma$, where γ is the mean half-width of the absorption line under atmospheric conditions. In this case at least one line must fall into the interval $\Delta\nu$. Here $\Delta\nu$ is the integration interval. The aerosol component of radiation extinction within the interval $\Delta\nu$ can be considered independent of ν and therefore τ_a is taken into account only in the final result after the transmission function due to gas absorption is calculated.

Different methods can be employed for calculating the transmission functions. For example the LOWTRAN method has become a most widely used.² It enables one to

calculate the transmission functions with resolution $\Delta\nu^* = 20 \text{ cm}^{-1}$ in the spectral range 0.25–28.6 μm with the step of 5 cm^{-1} for a rectangular instrumental contour $\tilde{g}(\nu, \nu')$ and $I_0(\nu')$ independent of ν' within $\Delta\nu^*$.

To calculate transmissions with poorer spectral resolution ($\Delta\lambda^* = 0.05 + 0.1 \mu\text{m}$) it is possible to employ a combined procedure³ based on different models of absorption bands assigned parametrically (from 2 to 4 parameters). In both these methods the absorption by several gases is taken into account using the rule of transmission product. The final result with the instrumental contour $\tilde{g}(\nu, \nu')$ (when $\Delta\nu \gg \Delta\nu^*$) taken into account can be obtained by the formula

$$T = \sum_{i=1}^C g_i T_i \Delta\nu^*,$$

where C is the number of nodes $\left(C = \left\lceil \frac{\Delta\nu}{\Delta\nu^*} \right\rceil \right)$, subscript i

denotes the number of the frequency ν_i , $\nu_i = \nu_1 + i \frac{\Delta\nu^*}{2}$.

The transmission can also be determined by the fast methods,^{4–5} where real spectrum of absorption of two or four bands is replaced by parametric models of bands. In so doing, the model parameters are found using an absorption line atlas. These methods have a common advantage of capability to calculate the transmissions with an arbitrary spectral resolution $\Delta\nu$ and, in addition, with more correct account for absorption by a gas mixture. By way of example, let us consider the model of an equivalent line.⁵

$$T(x, \gamma) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\left(-\frac{x\gamma^2}{t^2 + \gamma^2}\right) dt,$$

where

$$x = \frac{1}{2\pi} \left(\frac{\sum_{i=1}^N S_i}{N} \right)^2 \rho l;$$

$$\gamma = \frac{2\pi}{\Delta\nu^*} \frac{\left(\sum_{i=1}^N \sqrt{S_i \gamma_i} \right)^2}{\sum_{i=1}^N S_i \gamma_i}.$$

Here S_i and γ_i are the intensity and half-width of the i th line entering into the interval $\Delta\nu^*$, N is the number of absorption lines in the interval $\Delta\nu^*$. For the gas mixture, the parameters x and γ have the form

$$x = \frac{1}{2\pi} \frac{\sum_{j=1}^m \rho_j l \sum_{i=1}^{N_j} S_i^j}{\left(\sum_{j=1}^m \sqrt{\rho_j l} \sum_{i=1}^{N_j} \sqrt{S_i^j \gamma_j} \right)^2};$$

$$\gamma = \frac{2\pi}{\Delta\nu^*} \frac{\left(\sum_{j=1}^m \sqrt{\rho_j l} \sum_{i=1}^{N_j} \sqrt{S_i^j \gamma_j} \right)^2}{\sum_{j=1}^m \rho_j l \sum_{i=1}^{N_j} S_i^j},$$

where subscript j denotes the j th gas and m is the number of gases in the mixture.

Narrow-band transmission functions. The spectral resolution $\Delta\nu$ is comparable with the absorption linewidth. Such a situation occurs when a laser light source is used. In this case, $g(\nu, \nu')$ is in fact a spectral distribution of the laser radiation intensity. The transmission functions must be calculated using a line-by-line method. At present the software packages developed by different groups of scientists, e.g., FASCOD⁶ developed at the laboratory AFGL (USA), LARA⁷ (Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences), and others are available for users.⁸

Monochromatic transmission functions. If the emission line is much narrower than the absorption line, it is possible to employ a monochromatic approximation ($g(\nu, \nu') = \delta(\nu - \nu')$). In this case we have

$$T = e^{-K\rho l} e^{-\tau}.$$

2. INFORMATIVE SPECTRAL INTERVALS FOR OPTOACOUSTIC INSTRUMENTS

When an optoacoustic spectroscopy technique is used the relation of a signal measured with an optoacoustic detector (OAD) to gas concentrations is linear⁹

$$U(\nu) = \eta W_0(\nu) \int_{\Delta\nu} g(\nu, \nu') \left[\sum_{j=1}^m K_j(\nu') \rho_j + \beta(\nu) \right] d\nu', \quad (7)$$

where $U(\nu)$ is the signal at the OAD output, $W_0(\nu)$ is the radiation power at the input to the OAD cell, η is the calibration constant, m is the number of gases in the mixture, and $g(\nu, \nu')$ is the instrumental function of an OAD (normalized to unit) which, in general, has the form

$$g(\nu, \nu') = \frac{\tilde{g}(\nu, \nu') W_0(\nu')}{\int_{\Delta\nu} \tilde{g}(\nu, \nu') W_0(\nu') d\nu'}$$

where $\beta(\nu)$ is the absorption coefficient of interfering gases and background absorption.

Elements of the matrix G for response (7) are independent of a gas concentration and formulas (14) from Ref. 1 can be used for calculating the information length.

For a one-component mixture ($m = 1$) instead of Eq. (2), we obtain

$$L = B \bar{K} (\rho_2 - \rho_1);$$

$$\bar{K} = \int_{\Delta\nu} \tilde{g}(\nu, \nu') K(\nu') d\nu';$$

$$B = \eta W_0 / \sigma; \quad (9)$$

$$\sigma = \sqrt{\sigma_U^2 + (\delta_{W_0}^2 + \delta_\eta^2) (\eta W_0 (\bar{K} \rho_2 + \beta))^2}, \quad (10)$$

where δ_{W_0} and δ_η are relative errors of W_0 and η measurements.

Expression (10) is derived based on formula (7) (see Ref. 1) as well as the approximate account of the error of determining the calibration constant η .

For a multicomponent mixture of m gases, if n wavelengths are used (Eq. (14), Ref. 1), we obtain the expression for L

$$L = \sqrt{\sum_{i,j=1}^n (\rho_2 - \rho_1)_i (R^T V^{-1} R)_{ij} (\rho_2 - \rho_1)_j}, \quad (11)$$

where R is the n by m matrix with the elements

$$R_{ij} = W_0(\nu_i) \eta_i \bar{K}_{ij};$$

$$\bar{K}_{ij} = \int_{\Delta\nu} g(\nu_i, \nu') K_j(\nu') d\nu', \quad (12)$$

where R^T is the transposed matrix R and V is the diagonal matrix with the elements σ_i^2

$$\sigma_i^2 = \sigma_U^2(i) + (\delta_{W_0}^2 + \delta_\eta^2) \eta_i^2 W_0^2(i) \left[\sum_{j=1}^m \bar{K}_{ij} \rho_2(j) + \beta_1 \right]^2.$$

And, finally, in the problem on search for the atmospheric transmission windows for conducting the gas analysis of minor gases we have

$$L = B \sum_{j=1}^m \bar{K}_j \rho^{\max}(j),$$

where \bar{K}_j is determined by formula (12) and the value B is calculated using Eq. (9) in which

$$\sigma = \sqrt{\sigma_U^2 + (\delta_{W_0}^2 + \delta_\eta^2) \eta_i^2 W_0^2 \left[\sum_{j=1}^m \bar{K}_j \rho^{\max}(j) + \beta \right]^2}.$$

Formula (12) can be essentially simplified, if $g(\nu, \nu')$ is rectangular and $W_0(\nu') = \text{const}$ within $\Delta\nu$. In this case the absorption coefficient K_{ij} has the form (in approximation of the collisional broadening mechanism)

$$\bar{K}_{ij} = \frac{1}{\Delta\nu_i} \int_{\Delta\nu_i} K_j(\nu') d\nu' = \frac{1}{\Delta\nu_i} \sum_{l=1}^{N_j} S_l^j, \quad (12a)$$

where S is the intensity of the l th line of the j th gas within the interval $\Delta\nu_i$ and N_j is the number of lines of the j th gas within the interval $\Delta\nu_i$.

Another limiting case is a monochromatic approximation, for which it follows from Eq. (12) that

$$\bar{K}_{ij} = K_{ij} = K_j(\nu_i), \quad (12b)$$

where $K_j(\nu_i)$ is the monochromatic absorption coefficient of the j th gas at frequency ν_i .

3. LONG-PATH DIFFERENTIAL ABSORPTION LASER GAS ANALYZER

The method of differential absorption is one of the most promising methods for remote gas analysis.¹⁰ To perform this method two wavelengths are used: on (λ_{on}) and

off (λ_{off}) the absorption line. Information about the integral over the path gas content is extracted from the logarithm of signal ratio.

Consider a laser path gas analyzer. Let us assume that the laser radiation line is much narrower than the absorption line. Then the measured signals on (P^{on}) and off (P^{off}) the line can be related in the following manner

$$P^{\text{on}} = P^{\text{off}} \eta e^{-2l\Delta K} e^{-2\Delta\beta l}, \quad (13)$$

where

$$\Delta K = K_{\text{on}} - K_{\text{off}}, \quad \Delta\beta = \beta_{\text{on}} - \beta_{\text{off}},$$

$$\eta = (\eta_{\text{on}} P_0^{\text{on}}) / (\eta_{\text{off}} P_0^{\text{off}}).$$

Here η_{on} and η_{off} are the calibration constants of the measurement system at the wavelengths λ_{on} and λ_{off} which include a geometric factor with interception of a laser beam reflected from a target taken into account, the reflection coefficient of a target (a topographic object), the photodetector efficiency, the transmitter-receiver transmission coefficient; β_{on} and β_{off} are the effective extinction coefficients which takes into account the extinction of light by atmospheric aerosol and "foreign" gas absorption at the wavelengths λ_{on} and λ_{off} ; K_{on} and K_{off} are the absorption

coefficients of the gas under study; and, $\omega = \frac{1}{l} \int_0^l \rho(t) dt$ is the average over the path gas concentration.

The information length L is calculated by formula (17) from Ref. 1

$$L = \frac{P^{\text{off}} \eta}{\sigma} \exp(-2\Delta\beta l) [\exp(-2l\Delta K\omega_1) - \exp(-2l\Delta K\omega_2)], \quad (14)$$

where σ , with the account for Eq. (6a), has the form

$$\begin{aligned} \sigma &= \sqrt{\sigma_{\text{on}}^2 + \sigma_{\text{off}}^2 \eta^2 + \sigma_{\eta}^2 (P_0^{\text{off}})^2} \leq \\ &\leq \sqrt{\delta_{\text{on}}^2 (P_0^{\text{on}} \eta_{\text{on}})^2 + (\delta_{\text{off}}^2 + \delta_{\eta}^2) (\eta P_0^{\text{off}})^2}. \end{aligned} \quad (15)$$

By substituting Eq. (13) into (14) the expression for L can be rewritten in the form

$$\begin{aligned} L &= \frac{P^{\text{off}} \eta \exp(-2l\Delta K\omega_2) \exp(-2\Delta\beta l)}{\sigma} \{\exp[2l\Delta K(\omega_2 - \omega_1)] - 1\} = \\ &= \frac{P^{\text{on}}(\omega_2)}{\sigma} \{\exp[2l\Delta K(\omega_2 - \omega_1)] - 1\}, \end{aligned}$$

from where it follows that the value $B = P^{\text{on}}(\omega) / \sigma$ is the generalized index of the signal-to-noise ratio on the absorption line for $\omega = \omega_2$. The signal $P^{\text{on}}(\omega_2)$ is determined by formula

$$P^{\text{on}}(\omega_2) = \eta_{\text{on}} P_0^{\text{on}} \exp[-2l(K_{\text{on}}\omega_2 + \beta_{\text{on}})].$$

4. NUMERICAL EXPERIMENT

Let us now present some results of numerical simulations of the information length L for the three aforementioned methods of measuring gas concentration.

Spectrophotometric method. Consider a "monochromatic" case. Assuming in Eqs. (2) and (3), that $\rho_1 = 0$ and introducing the designation $\tau_{\text{ab}} = K\rho_2 l = K\rho l$,

$\tau = \beta l$ we obtain the following expression for L (with the account for Eq. (6a))

$$L = B [1 - \exp(-\tau_{\text{ab}})] = B_0 \exp(-\tau) [1 - \exp(-\tau_{\text{ab}})], \quad (16)$$

where

$$B_0 = \frac{1}{\sqrt{d_l^2 + d_{l_0}^2 + d_g^2}}.$$

Here B_0 is the generalized index of the signal-to-noise ratio of the entire measuring system, τ_{ab} is the optical thickness of the gas under study, τ is the optical thickness of the "interfering" gases and aerosol.

Depicted in Fig. 1 are plots of L vs τ_{ab} for different values of τ with fixed $B_0 = 10$. As could be expected, the information length L decreases with increase of contribution coming from interfering gases (with increase of τ) and thus the classification error ε increases. In addition, one more peculiarity in the τ_{ab} dependence of L is observed, i.e., the curves L tend to saturation with increasing τ_{ab} . For larger values of τ , the "saturation" occurs at smaller τ_{ab} . When B_0 increases the curves L are "saturated" at larger τ_{ab} . This is an important result for practice. The main point here is that the system sensitivity to the absorption coefficient $\alpha = K\rho$ is "saturated".

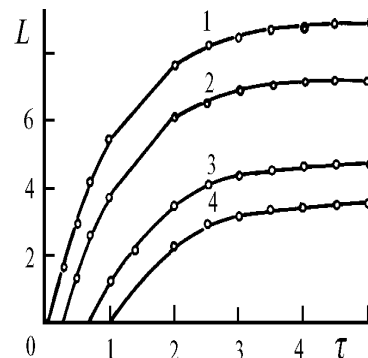


FIG. 1. A plot of the information length L vs optical thickness τ of the gas under study, for different optical depths of the interfering components: 1) $\tau = 0.01$, 2) 0.03 , 3) 0.07 , and 4) 1 .

Figure 2 shows a plot of L vs the path length l for different values of the information parameter α and the absorption coefficient of interfering gases β . Here the curves L possess extremum, i.e., there is an optimal path length l for which the measurement conditions are most favourable.

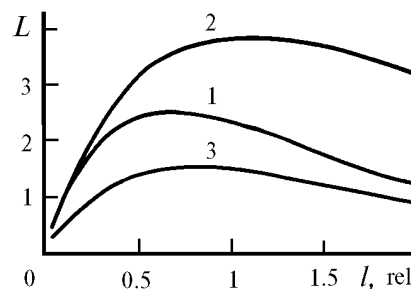


FIG. 2. A plot of the information length L vs the path length l for the spectrophotometric method for $B_0 = 10$: 1) $\alpha = 1$ and $\beta = 1$, 2) $\alpha = 1$ and $\beta = 0.5$, and 3) $\alpha = 0.5$ and $\beta = 1$.

The optoacoustic method. Assuming in formulas (8)–(10) that $\rho_1 = 0$, and $\rho_2 = \rho$ we obtain the expression for L

$$L = B_0 \bar{K}\rho / (\bar{K}\rho + \beta), \tag{17}$$

where

$$B_0 = \frac{1}{\sqrt{\delta_U^2 + \delta_{W_0}^2 + \delta_\eta^2}}.$$

Below are given calculational results on minimum–detectable concentrations providing $L = L_0 = 3.3$ for quasimonochromatic mode of measurements ($\bar{K} = K$). Table I lists the results of the ρ_{\min} simulation at the CO₂–laser transitions. The parameters of the measuring system typical of this class of instruments have been used in simulations, $\delta_U = \delta_{W_0} = \delta_\eta = 5\%$; the value of the background absorption coefficient $\beta_{bn} = 3 \cdot 10^{-8} \text{ cm}^{-1}$. Presented in this table also are the values ρ_{\min} obtained in Ref. 11. It can be seen that the considered ρ_{\min} are in satisfactory agreement with the results from Ref. 11.

TABLE I. Comparison of the calculated minimum–detectable concentrations and those measured in Ref. 11 for an optoacoustic method.

Gas	Laser transition	K, cm ⁻¹ ·atm ⁻¹ (Ref. 10)	ρ_{\min} , ppb	ρ_{\min} , ppb (Ref. 10)
C ₂ H ₄	10 P(14)	3.26·10 ¹	4.0·10 ⁻¹	7.0·10 ⁻¹
H ₂ O	10 R(20)	7.96·10 ⁻⁴	1.8·10 ⁴	2.0·10 ⁴
C ₆ H ₆	9 P(30)	3.26·10 ¹	7.4	1.0·10 ¹

The long path differential absorption method. Based on Eqs. (14) and (15) for $\omega_1 = 0$ and $P_0^{\text{on}} = P_0^{\text{off}}$ we have

$$L = B_0 \exp(-2\Delta\beta l) [1 - \exp(-\tau_{\text{ab}})], \tag{18}$$

where $B_0 = \frac{1}{\sqrt{\delta_{\text{on}}^2 + \delta_{\text{off}}^2 + \delta_\eta^2}}$; $\tau_{\text{ab}} = 2\Delta K\omega l$ is the optical thickness of the studied gas.

Expression (18), in its form and sense, coincides with Eq. (16). Therefore, the conclusions drawn from Eq. (18) with respect to the dependence of L on τ_{ab} and path length l are the same as those from Eq. (16).

Let us now present some results of simulating the minimum–detectable concentration for a CO₂–laser–based differential absorption measurement system. Table II gives our results for ρ_{\min} for the pairs of wavelengths listed in the second column. The errors in signals P^{on} and P^{off} are

assigned to be 5% and $\delta_g = 0\%$. In the last column are given the values ρ_{\min} taken from Ref. 12. Our results for ρ_{\min} exceed by a factor of 2–3 the values from Ref. 12. This difference is explained by the fact that in Ref. 12, the statistical nature of signal is not taken into account when calculating minimum–detectable concentrations. The complete account of not only physical regularities but also of the statistical nature of signals enables one to obtain more realistic estimates of minimum–detectable concentrations for the given measuring system.

TABLE II. Comparison of the calculated minimum–detectable concentrations and those measured in Ref. 12 for a long–path gas analyzer.

Gas	Laser transitions	ΔK , cm ⁻¹ ·atm ⁻¹	ρ_{\min} , ppb	ρ_{\min} , ppb (Ref. 12)
NH ₃	10 R(30) 10 R(18)	7.80	3.0	1.0
H ₂ O	10 R(20) 10 R(18)	6.60·10 ⁻⁵	2.4·10 ⁴	1.7·10 ⁴
O ₃	9 P(14) 9 P(22)	1.03·10 ¹	1.5·10 ¹	5.0
C ₂ H ₄	10 P(14) 10 P(22)	3.34	5.0	2.0

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