SELECTION OF THE INFORMATIVE SPECTRAL SECTIONS FOR THE SOLUTION OF GAS ANALYSIS PROBLEMS WITH THE HELP OF AN OPTOACOUSTIC DETECTOR

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Received March 16, 1990

An algorithm for selecting the informative spectral sections for an optoacoustic gas analyzer is presented. The algorithm is based on Bayes risk. The optimal spectral sections for different gaseous components in the lasing region of a CO_2 laser are determined. The results are compared with published data.

INTRODUCTION

In the design and development of optical devices and systems for gas analysis the optimal spectral sections must be selected. In the problems of gas analysis based on absorption spectra the sections are chosen in the absorption bands so as to guarantee maximum sensitivity and selection with respect to the gases. The development of systems for recording and storing on magnetic carriers information about the absorption spectra of gases as well as the development of computer technology have made it possible to automate the search for the informative spectral sections. Without the appropriate mathematical algorithms, however, this work is very laborious and inefficient.

In this paper we describe a mathematical algorithm for selecting the optimal spectral sections for an optoacoustic gas analyzer and we present the results of modeling of the probability of error in detecting gaseous components with the help of an optoacoustic detector (OAD) at different wavelengths of the CO_2 laser. The computed minimum detectable concentrations of gases for different conditions are compared with the published data.

FORMULATION OF THE PROBLEM

We shall study a gas mixture only one component of which is to be analyzed. We shall regard the other gases in the mixture as background gases. The absorption spectra are measured with an OAD. The source is a laser with a quasimonochromatic emission spectrum (the emission line is much narrower than the absorption line).

The relation between the measured signal and the gas concentration is given by the relation[1]

$$\bar{y} = y_0 \eta \, [K \cdot \rho + \beta], \qquad (1)$$

where $\bar{y}$ is the average value of the measured optoacoustic signal, y_0 is the radiation power absorbed in the cell of the OAD, η is the .sensitivity of the OAD, K is the coefficient of absorption per unit concentration of gas; ρ is the concentration of the gas being studied, and β is the volume absorption coefficient of the other gases present in the gas mixture (it can also include the aerosol component of extinction). In addition β_b corresponding to the background signal (no absorbing gases in the AOD cell) is also included in β.

From the mathematical standpoint the problem of selecting the informative spectral sections can be regarded as a problem of distinguishing gaseous objects based on the measured optoacoustic signals.

BAYESIAN CRITERION OF DETECTION. GENERAL ALGORITHM

We shall construct the signal-processing algorithm for signals at the output of the optoacoustic detector (post-detector detection).

Apart from the measured signal y, we shall also assume that the sensitivity of the OAD η (which is measured in an independent experiment), the gas concentration ρ, and the volume absorption coefficient β are random quantities. This determines the statistical approach to the solution of the problem posed. Previously[2-4] we studied this problem from the standpoint of identifying the gaseous composition of a mixture based on the measured absorption spectra. The problem of lidar detection of minor gas components based on the measured Raman scattering spectra was solved in Refs. 5–6. In contradistinction to these problems, in this paper we shall focus on the investigation of the risk function or the detection error. The likelihood function itself, to calculate which it is necessary to have the values of the measured signals, will not be studied here, since the problem we have posed is connected with determining the informative section and the minimum detectable concentrations at the stage of design of the optoacoustic gas analyzer (before the signals are measured).

We shall study the general algorithm for the Bayes criterion of detection. Consider two classes of

states Y_1 and Y_2, to one of which y can belong. The detection problem reduces to checking the statistical hypothesis H_1 that the measured parameter y belongs to the class of final states $Y_{H_1} \equiv Y_1$ as opposed to the alternative H_2 according to which the measured parameter y belongs to the class $Y_{H_2} \equiv Y_2$. The classes of states Y_1 and Y_2 are fixed by the conditional probability densities $P(y|H_1)$ and $P(y|H_2)$. The fact that the signal y belongs to the class of results Y_1 is, in turn, connected with the fact that the concentration of the gas ρ belongs to the class of states X_i, $i = 1, 2$.

One of the main characteristics determining the quality of the decision rule is the average risk (or the classification error). The expression for the average risk has the form[7]

$$R = qW_{11} + pW_{21} + q\left(W_{12} - W_{11}\right)\cdot\varepsilon_1 -$$
$$- p\left(W_{21} - W_{22}\right)\cdot\left(1 - \varepsilon_2\right), \tag{2}$$

where W_{ij} are the elements of the matrix of losses (W_{11}, W_{22} are the costs of a correct solution when the hypothesis H_1 and H_2, respectively, are adopted; W_{12} is the cost of an error of the first kind, i.e., adopting the solution $y \in Y_2$, when in reality $y \in Y_2$; is the price of an error of the second kind); q and $p = 1 - q$ are the *a priori* probabilities of the fact that the unknown parameter ρ belongs to nonintersecting classes of states X_1 and X_2. The probabilities of errors of the first kind ε_1 and errors of the second kind ε_2, appearing in Eq. (2), are determined by the following formulas:[7]

$$\varepsilon_1 = \int_{X_1}\omega_1(\rho)\int_{Y_2} P\left(y|\rho \in X_1\right)\iint \upsilon(\eta)\varphi(\beta)\ d\eta d\beta d\rho dy, \tag{3}$$

$$\varepsilon_2 = \int_{X_2}\omega_2(\rho)\int_{Y_1} P\left(y|\rho \in X_2\right)\iint \upsilon(\eta)\varphi(\beta)\ d\eta d\beta d\rho dy. \tag{4}$$

where $\upsilon(\eta)$, $\varphi(\beta)$ are the probability distributions of the random quantities η and β; $\omega_1(\rho)$, $\omega_2(\rho)$ are the *a priori* distributions of the random quantity ρ in the hypotheses H_1 and H_2, respectively. Since η and β are the "interfering" parameters, the distributions $\upsilon(\eta)$ and $\varphi(\beta)$ in both hypotheses were assumed to be identical.

To calculate the probabilities of the errors ε_1 and ε_2 based on the formulas (3) and (4) it is necessary to determine the boundary of the mutually complementary regions Y_1 and Y_2 or, in other words, to find the intervals Y_1 and Y_2. The interval Y_1 (or Y_2) is determined from the condition of minimum average risk R and is found from the following equation:[7,8]

$$q\left(W_{12} - W_{11}\right)\int_{X_1}\omega_1(\rho)\iint \upsilon(\eta)\varphi(\beta)P\left(y|\rho \in X_1\right)d\eta d\beta d\rho =$$
$$= p\left(W_{21} - W_{22}\right)\times$$
$$\times\int_{X_2}\omega_2(\rho)\iint \upsilon(\eta)\varphi(\beta)P\left(y|\rho \in X_2\right)\ d\eta d\beta d\rho. \tag{5}$$

The value $y = u$ satisfying this equation is the boundary of the intervals Y_1 and Y_2.

Thus if the distributions $\omega_1(\rho)$, $p(y|\rho \in X_1)$, $i = 1, 2$, $\upsilon(\eta)$, $\varphi(\beta)$ are known, the average risk owing to the adoption of one of the hypotheses $H_1 - y \in Y_1$ or $H_2 - y \in Y_2$ (correspondingly, $\rho \in X_1$ or $\rho \in X_1$) can be calculated from the formulas (2)–(5). It should be noted that in calculating the risk using the formulas (2)–(5) the measured signals themselves are not required, and therefore the calculations can be performed before the measurements are made.

SEARCH CRITERION FOR OPTIMAL SPECTRAL SECTIONS

We shall now determine the search criterion for informative spectral sections. The distributions $p(y|\rho \in X_1)$ are functions of the mass absorption coefficient K, which, in turn, is determined by the spectroscopic information and depends on the wavelength. The absorption coefficient β of the background gases also depends on the wavelength.

Thus the average risk R is a function of the wavelength λ. As the wavelength varies over the selected spectral range for the given values of $\bar{\rho}_1$, $\bar{\rho}_2$, $\sigma_{\rho_1}^2$, $\sigma_{\rho_2}^2$ (determining the *a priori* distributions $\omega_1(\rho)$ and $\omega_2(\rho)$) and concentrations of the background gases, which appear in β, the value of the risk will also vary. The wavelength λ_0 for which the risk R is minimum in some wavelength range will be the optimal wavelength for the gas ρ under study. The criterion of optimality can be written in the form

$$R(\lambda) \underset{\lambda}{\longrightarrow} \min, \tag{6}$$

or

$$R(\lambda) \leq R_0, \tag{6a}$$

where R_0 is the threshold value of the average risk.

For wavelength-tunable lasers (for example, CO_2 lasers, as well as others) it is most convenient to minimize R not with respect to λ, but rather with respect to the known values $K_1 = K(\lambda_1)$.

CALCULATION OF THE AVERAGE RISK

The calculation of the average risk R reduces to calculating the probabilities of the errors ε_1 and ε_2 of the first and second kind. In order to calculate the integrals ε_1 and ε_2 analytically it is necessary to know the form of the probability distributions of all parameters appearing in Eqs. (3) and (4). We shall study these distributions.

1. We shall assume that the conditional distributions $P(y|H_1)$ in both hypotheses are normal distributions with the parameters $\tilde{M}_1$, $\sigma_{y_1}^2$, where $\tilde{M}_1$, $\sigma_{y_1}^2$ are the average values and the variances ($i = 1, 2$).

2. The distribution $\upsilon(\eta)$ is a normal distribution with the parameters M_η and σ_η^2.

3. We shall approximate the *a priori* distribution $\omega_1(\rho)$ by the following types of distributions: a) δ-function $\omega_1(\rho) = \delta(\rho - \bar{\rho})$; b) normal distribution with the parameters $\bar{\rho}$ and σ_ρ^2; and, c) gamma distribution $\Gamma(a, b)$ with the parameters $a = \bar{\rho} / \sigma_\rho^2$ and $b = \bar{\rho}^2 \sigma_\rho^2$.

4. We shall assume that the distribution $\omega_2(\rho)$ is a δ-function $\omega_2(\rho) = \sigma(\rho - \bar{\rho}_2)$ with the parameter $\bar{\rho}_2 = 0$.

5. The distribution $\varphi(\beta)$ is a δ-function.

As a result we obtain the following expressions for the error ε_1.

The case (a)

$$\varepsilon_1 = \frac{1}{2}\left[1 - \Phi(g_1)\right]. \tag{7}$$

The case (b)

$$\varepsilon_1 = \frac{c}{\sqrt{2\pi}\,\sigma_\rho} \times$$

$$\times \int_0^\infty \exp\left\{-\frac{(\rho - \bar{\rho})^2}{2\sigma_\rho^2}\right\}\frac{1}{2}\left[1 - \Phi(g_1(\rho))\right]d\rho. \tag{8}$$

The case (c)

$$\varepsilon_1 = \frac{a^b}{\Gamma(b)}\int_0^\infty \rho^{b-1}\,e^{-a\rho}\,\frac{1}{2}\left[1 - \Phi(g_1(\rho))\right]d\rho. \tag{9}$$

The error ε_2 for all cases is calculated based on the formula

$$\varepsilon_2 = \frac{1}{2}\left[1 - \Phi(g_2)\right]. \tag{10}$$

In Eqs. (7)–(10) $\Phi(g)$ is the error function

$$\left(\Phi(g) = \frac{2}{\sqrt{\pi}}\int_0^g e^{-t^2}dt\right);$$

$\Gamma(b)$ is the gamma function; c is a normalization constant $(c = 2 / (1 + \Phi(\bar{\rho} / \sqrt{2}\sigma_\rho)))$ for $\bar{\rho} / \sigma_\rho > 3$, $c \simeq 1$. The parameters g_1, $g_1(\rho)$, and g_2 are

$$g_1 = \frac{M_1 - u}{\sqrt{2}\,\sigma_1}\;;\;\; g_1(\rho) = \frac{E_1 - u}{\sqrt{2}\,\Sigma_1}\;;\;\; g_2 = \frac{u - M_2}{\sqrt{2}\,\sigma_2}, \tag{11}$$

where

$$M_1 = M_\eta y_0(K\bar{\rho} + \beta),\; M_2 = M_\eta y_0 \beta,\; E_1 = M_1 + M_\eta y_0 \upsilon, \tag{12}$$

$$\Sigma_1 = \sigma_1\left\{1 + \frac{1}{\sigma_1^2}\sigma_\eta^2\,y_0^2(K\bar{\rho} + \beta)^2 \times\right.$$

$$\left.\times\left[\left[1 + \frac{\upsilon}{K\bar{\rho} + \beta}\right]^2 - 1\right]\right\}^{1/2}, \tag{13}$$

$$\sigma_1 = \left\{\sigma_{y_1}^2 + \sigma_\eta^2\,y_0^2(K\bar{\rho} + \beta)^2\right\}^{1/2},$$

$$\sigma_2 = \left\{\sigma_{y_2}^2 + \sigma_\eta^2\,y_0^2\,\beta^2\right\}^{1/2},\;\; \upsilon = K(\rho - \bar{\rho}), \tag{14}$$

where u is the boundary of the interval Y_1 and Y_2, determined from the solution of Eq. (5), which assumes the following form after the distributions $p(y|\rho \in X_1)$, $\upsilon(\eta)$ and $\varphi(\beta)$, given above, are substituted into it and the integrations over $d\eta$ and $d\beta$ are performed:

$$q(W_{12} - W_{11}) \times$$

$$\times \int_{X_1} \omega_1(\rho)\frac{1}{\sqrt{2\pi}\,\Sigma_1}\exp\left\{-\frac{1}{2\Sigma_1^2}(y - E_1(\rho))^2\right\}d\rho =$$

$$= p(W_{21} - W_{22})\frac{1}{\sqrt{2\pi}\,\sigma_2}\exp\left\{-\frac{1}{2\sigma_2^2}(y - M_2)^2\right\}. \tag{15}$$

For $\omega_1(\rho) = \delta(\rho - \bar{\rho})$, $\Sigma_1 \to \sigma_1$, $E_1 \to M_1$.

We note that the formulas (7)–(10) and Eq. (15) are valid when the following conditions are satisfied:

$$\frac{M_\eta}{\sqrt{2}\,\sigma_\eta}\frac{\sigma_{y_2}}{\sigma_2} > 3, \qquad \frac{M_\eta}{\sqrt{2}\,\sigma_\eta}\frac{\sigma_{y_1}}{\Sigma_1} > 3. \tag{16}$$

The formulas obtained make it possible to determine the informative spectral sections for the solution of the problem of detection when two hypothesis are checked: H_2 — the gas is not present in the mixture and H_1 — the gas is present in the mixture. In our opinion, it is the choice of precisely these hypotheses that best corresponds to

the solution of the problem posed. Indeed, if the magnitude of the risk for some wavelength $\lambda R(\lambda) \leq R_0(\lambda)$, where $R_0(\lambda)$ is the threshold value, then the device should "feel" the presence of the gas in the mixture, when in reality the gas is present in the mixture and, vice versa, the device will not "feel" the gas when in reality it is not present in the mixture or its concentration is much lower than assumed in the hypothesis H_1. The value of the concentration of the gas, for which $R(\lambda, \rho) = R_0$, can be regarded as the minimum detectable concentration at the given wavelength λ for the given characteristics of the OAD.

SEARCH FOR THE INFORMATIVE WAVELENGTHS IN THE SPECTRAL LASING RANGE OF A CO LASER

As an example we shall study the spectral lasing of a tunable CO_2 laser. Table I gives the transitions of the CO_2 laser and the wavelengths and absorption coefficients of six gases. The lasing wavelengths were taken from Ref. 9. We calculated the absorption coefficients of H_2O, CO_2, and O_3 with the help of the LARA package[10] based on data from the atlas Ref. 11. The data on the absorption coefficients of the other gases were taken from sources in the literature.[9,12–15]

The absorption coefficient β for the jth gas studied was calculated from the formula

$$\beta_j = \sum_{1 \neq j}^{4} K_1 \rho_1^b + K_{H_2O} \rho_{H_2O} + \alpha_c + \alpha_a + \beta_p, \tag{17}$$

where ρ_c^b are the background values of the concentrations, presented in Table II; α_c is the continuous-absorption coefficient of H_2O, calculated from the empirical formula of Ref. 17; and, α_a is the aerosol extinction coefficient, taken from Ref. 18. The coefficients of selective absorption K_{H_2O} are given in Table I. The values of the moisture content were set equal to 3.0 and 14 g/m^3 in order to simulate different levels of the "background" absorption. The background absorption coefficient β_b, determining the background signal when no absorbing gases are present in the OAD cell, was assumed to be equal to 10^{-7} cm^{-1} (Ref. 19).

The signals y were calculated for typical values of the parameters of the laser optoacoustic system: $y_0 = 0.1$ W, $\eta = 100$ V$/($W $\cdot$ cm$^{-1})$. The error in measuring the quantities y and η was assumed to be equal to 5%, i.e., $\sigma_{y_i} = 0.05 M_1$ $(i = 1, 2)$ where M_1 are determined by the expressions (12) and $\sigma_\eta = 0.05 M_\eta$.

The risk was calculated for the following values of the elements of the matrix of losses: $W_{11} = W_{12} = 0$; $W_{12} = W_{11} = 1$. The *a priori* probabilities were assumed to be equal to one another; $q = p = 0.5$. The distribution $\omega_1(\rho)$ was approximated by the normal law with the parameter $\bar\rho$ and $\sigma_\rho = 0.1\bar\rho$.

TABLE I. Absorption coefficients in atm^{-1}cm^{-1}.

Transition	Wavelength, μm	H_2O*	CO_2*	NH_3 of Refs. 12–14	O_3*	C_2H_4 of Ref. 9	C_6H_6 of Ref. 15
9R(30)	9.220	$2.905 \cdot 10^{-6}$	$1.999 \cdot 10^{-3}$	$7.25 \cdot 10^{+1}$	$8.787 \cdot 10^{-2}$	$1.50 \cdot 10^{-1}$	$9.3 \cdot 10^{-4}$
9R(20)	9.271	$1.966 \cdot 10^{-6}$	$3.358 \cdot 10^{-3}$	$2.70 \cdot 10^{-2}$	$9.367 \cdot 10^{-2}$	$1.13 \cdot 10^{-1}$	$9.3 \cdot 10^{-4}$
9P(10)	9.473	$1.231 \cdot 10^{-4}$	$2.844 \cdot 10^{-3}$	$3.60 \cdot 10^{-1}$	$5.725 \cdot 10^{+0}$	$4.27 \cdot 10^{-1}$	$6.33 \cdot 10^{-1}$
9P(12)	9.488	$1.614 \cdot 10^{-6}$	$3.046 \cdot 10^{-3}$	$9.40 \cdot 10^{-1}$	$1.054 \cdot 10^{+1}$	$1.88 \cdot 10^{-1}$	$5.53 \cdot 10^{-1}$
9P(14)	9.504	$3.603 \cdot 10^{-6}$	$3.174 \cdot 10^{-3}$	$3.10 \cdot 10^{-1}$	$1.171 \cdot 10^{+1}$	$1.76 \cdot 10^{-1}$	$7.54 \cdot 10^{-1}$
9P(24)	9.586	$1.223 \cdot 10^{-6}$	$2.661 \cdot 10^{-3}$	$4.30 \cdot 10^{-1}$	$4.403 \cdot 10^{-1}$	$4.52 \cdot 10^{-1}$	$4.52 \cdot 10^{-1}$
9P(26)	9.603	$1.621 \cdot 10^{-6}$	$2.385 \cdot 10^{-3}$	$1.00 \cdot 10^{-1}$	$5.244 \cdot 10^{+0}$	$3.02 \cdot 10^{-1}$	$5.03 \cdot 10^{-1}$
9P(28)	9.621	$5.689 \cdot 10^{-5}$	$2.092 \cdot 10^{-3}$	$6.00 \cdot 10^{-2}$	$7.966 \cdot 10^{+0}$	$2.36 \cdot 10^{-1}$	$1.13 \cdot 10^{+0}$
9P(30)	9.639	$9.758 \cdot 10^{-7}$	$1.793 \cdot 10^{-3}$	$8.20 \cdot 10^{-2}$	$5.084 \cdot 10^{+0}$	$1.26 \cdot 10^{+0}$	$2.01 \cdot 10^{+0}$
10R(20)	10.247	$6.665 \cdot 10^{-4}$	$2.532 \cdot 10^{-3}$	$3.60 \cdot 10^{-1}$	$8.687 \cdot 10^{-2}$	$1.34 \cdot 10^{+0}$	$3.02 \cdot 10^{-3}$
10R(18)	10.260	$4.406 \cdot 10^{-6}$	$2.661 \cdot 10^{-3}$	$2.30 \cdot 10^{-1}$	$7.486 \cdot 10^{-2}$	$1.01 \cdot 10^{+0}$	$3.52 \cdot 10^{-3}$
10R(10)	10.318	$7.063 \cdot 10^{-7}$	$2.294 \cdot 10^{-3}$	$6.30 \cdot 10^{-1}$	$2.382 \cdot 10^{-2}$	$1.63 \cdot 10^{+0}$	$1.76 \cdot 10^{-3}$
10R(8)	10.333	$1.284 \cdot 10^{-6}$	$2.018 \cdot 10^{-3}$	$2.46 \cdot 10^{+0}$	$1.631 \cdot 10^{-2}$	$1.26 \cdot 10^{+0}$	$1.38 \cdot 10^{-3}$
10P(12)	10.513	$7.656 \cdot 10^{-7}$	$2.275 \cdot 10^{-3}$	$5.70 \cdot 10^{-1}$	$7.106 \cdot 10^{-4}$	$5.03 \cdot 10^{+0}$	$8.29 \cdot 10^{-4}$
10P(14)	10.532	$3.145 \cdot 10^{-6}$	$2.404 \cdot 10^{-3}$	$8.10 \cdot 10^{-1}$	$7.086 \cdot 10^{-5}$	$3.27 \cdot 10^{+0}$	$6.80 \cdot 10^{-4}$
10P(16)	10.551	$1.689 \cdot 10^{-5}$	$2.440 \cdot 10^{-3}$	$5.30 \cdot 10^{-1}$	$1.553 \cdot 10^{-5}$	$8.04 \cdot 10^{+0}$	$6.30 \cdot 10^{-4}$
10P(30)	10.697	$8.031 \cdot 10^{-7}$	$1.359 \cdot 10$	$8.50 \cdot 10^{-1}$	$2.280 \cdot 10^{-7}$	$1.59 \cdot 10^{+0}$	$3.77 \cdot 10^{-4}$
10P(32)	10.718	$1.254 \cdot 10^{-7}$	$1.148 \cdot 10^{-3}$	$1.58 \cdot 10^{+1}$	$3.400 \cdot 10^{-7}$	$1.38 \cdot 10^{+0}$	$2.51 \cdot 10^{-4}$

*We calculated the absorption coefficients of H_2O, CO_2, and O_3 from the data given in Ref. 11.

TABLE II. The background values of the concentrations of the gases in ppmv

Gas	CO_2 of Ref. 16	NH_3 of Ref. 16	O_3 of Ref. 16	$C_2H_4^*$ of Ref. 9	C_6H_6 of Ref. 9
ρ^P, ppmv	330	5.0—4	2.66—2	2.0—2	5.0—3

*The typical values of the concentrations of C_2H_4 and C_6H_6 are presented in Table II. According to the data in Ref. 9, taken from different sources in the literature, the expected values of the concentrations of the gases C_2H_4 and C_6H_6 in an urban location are equal to (1–100) ppbv and (5–150) ppbv, respectively.

TABLE III. The concentrations of the gases in ppm for $R = 0.05$, $\delta_y = \delta_\eta = 5\%$, $\delta_\rho = 10\%$, $\beta_b = 10^{-2}$ km^{-1}; 1 — $\rho_{H_2O} = 3$ g/m^3; 2 — $\rho_{H_2O} = 14$ g/m^3.

Transition	CO_2		NH_3		O_3		C_2H_4		C_6H_6	
	1	2	1	2	1	2	1	2	1	2
9R(30)	$0.956 \cdot 10^2$	$0.317 \cdot 10^3$	$0.505 \cdot 10^{-2}$	0.0111	—	—	—	—	—	—
9R(20)	$0.541 \cdot 10^2$	$0.186 \cdot 10^3$	—	—	—	—	—	—	—	—
9P(10)	$0.119 \cdot 10^3$	$0.414 \cdot 10^3$	—	—	0.0979	0.245	—	—	0.952	2.280
9P(12)	$0.884 \cdot 10^2$	$0.240 \cdot 10^3$	—	—	0.0451	0.089	—	—	1.000	1.840
9P(14)	$0.884 \cdot 10^2$	$0.237 \cdot 10^3$	—	—	0.0418	0.082	—	—	0.764	1.380
9P(24)	$0.743 \cdot 10^2$	$0.252 \cdot 10^3$	—	—	—	—	—	—	0.987	2.030
9P(26)	$0.980 \cdot 10^2$	$0.297 \cdot 10^3$	—	—	0.0796	0.170	—	—	0.907	1.850
9P(28)	$0.144 \cdot 10^3$	$0.454 \cdot 10^3$	—	—	0.0549	0.136	—	—	0.439	1.010
9P(30)	$0.133 \cdot 10^3$	$0.399 \cdot 10^3$	—	—	0.0724	0.166	0.3160	0.6950	0.200	0.438
10R(20)	$0.290 \cdot 10^3$	$0.134 \cdot 10^4$	—	—	—	—	—	—	—	—
10R(18)	$0.671 \cdot 10^2$	$0.282 \cdot 10^3$	—	—	—	—	0.4180	0.9830	—	—
10R(10)	$0.776 \cdot 10^2$	$0.326 \cdot 10^3$	—	—	—	—	0.2350	0.5840	—	—
10R(8)	$0.875 \cdot 10^2$	$0.371 \cdot 10^3$	$0.148 \cdot 10^{+0}$	0.3810	—	—	0.2840	0.7390	—	—
10P(12)	$0.862 \cdot 10^2$	$0.351 \cdot 10^3$	—	—	—	—	0.0758	0.1960	—	—
10P(14)	$0.147 \cdot 10^3$	$0.403 \cdot 10^3$	—	—	—	—	0.0121	0.0308	—	—
10P(16)	$0.932 \cdot 10^2$	$0.363 \cdot 10^3$	—	—	—	—	0.0510	0.1330	—	—
10P(30)	$0.130 \cdot 10^3$	$0.600 \cdot 10^3$	—	—	—	—	0.1860	0.5870	—	—
10P(32)	$0.155 \cdot 10^3$	$0.713 \cdot 10^3$	$0.179 \cdot 10^{-1}$	0.0585	—	—	0.2140	0.7060	—	—

We shall now analyze the results obtained. Table III gives the values of the gas concentrations, for which the risk R is equal to 0.05. One can see from Tables II and III that the background concentrations can be detected from the measured optoacoustic signals with a risk of 0.05 only for CO_2 on all transitions of the CO_2 laser when the moisture content is low in the volume studied; when the moisture content is high, the background CO_2 can be detected only on ten transitions. It is easy to see that H_2O is the main gas that interferes with the detection of CO_2. This can be seen from Table I — at the transitions of the CO_2 laser for which K_{H_2O} assumes its highest values, ρ_{CO_2} also assumes its highest values.

The main interfering gases in detecting NH_3, O_3, C_2H_4, and C_6H_6 are H_2O and CO_2. Of the four remaining gases the only gas that can be detected at the background level is C_2H_4 (the transition 10P(14)). On the transitions 10P(12) and 10P(16) the values of the detected concentrations of C_2H_4 are (75.8–196) ppb and (51–133) ppb with moisture content in the air of (3–14) g/m^3; for C_6H_6 we call attention to the transition 9P(30), on which the detected concentrations are equal to (200–438) ppb.

We shall now compare the results obtained with the published data. In Ref. 20 the optoacoustic system is described and the sensitivity with respect to absorption $\beta_b = 8.42 \cdot 10^{-9}$ cm^{-1} is given. However the real sensitivity will be limited by the presence of "background" gases (H_2O and CO_2) as well as the aerosol component in the gas mixture.

Table IV gives the values of ρ^p_{min} for six gases, calculated with the two main background gases present — H_2O and CO_2 (columns 6 and 7) (the effect of the

others can be neglected) and when atmospheric aerosol is present in the volume studied (columns 4 and 5). In order to make an adequate comparison of the results for ρ_{min}^p we employed the absorption coefficients K from Ref. 20. Since the concentration of the main "background" gas H_2O is not indicated in Ref. 20, the values

of ρ_{min}^p for ρ_{H_2O}, equal to 3 and 14 g/m^3, are given in Table IV. One can see that ρ_{min}^e (Ref. 20) for five gases (NH_3, O_3, C_2H_4, C_6H_6, and O_2) fall within our range' of values of ρ_{min}^p for $\rho_{H_2O} = 3$ and 14 g/m^2 and in the presence of the aerosol component (columns 4 and 5).

TABLE IV. The minimum detectable concentrations of gases, $\delta_y = \delta_\eta = 5\%$, $\delta_\rho = 10\%$, $R = 0.005$, $\beta = \alpha_{H_2O} + \alpha_{CO_2} + \beta_b$, $\beta_b = 10^{-3}$ km^{-1}.

The Gas	The OQG line	$K,$ $cm^{-1}atm^{-1}$ (Ref.20)	ρ_{min}^c, ppm *		ρ_{min}^c, ppm		ρ_{min}^e, ppm of Ref. 20
			$\rho_{H_2O} = 3g/m^3$	$\rho_{H_2O} = 14g/m^3$	$\rho_{H_2O} = 3g/m^3$	$\rho_{H_2O} = 14g/m^3$	
1	2	3	4	5	6	7	8
NH_3	9R(30)	75	$0.453 \cdot 10^{-2}$	$0.104 \cdot 10^{-1}$	$0.305 \cdot 10^{-2}$	$0.895 \cdot 10^{-2}$	$0.110 \cdot 10^{-1}$
O_3	9P(8)	12.7	$0.326 \cdot 10^{-1}$	$0.703 \cdot 10^{-1}$	$C.229 \cdot 10^{-1}$	$0.605 \cdot 10^{-1}$	$0.665 \cdot 10^{-1}$
C_2H_4	10P(14)	29.1	$0.127 \cdot 10^{-1}$	$0.338 \cdot 10^{-1}$	$0.967 \cdot 10^{-2}$	$0.308 \cdot 10^{-1}$	$0.263 \cdot 10^{-1}$
C_6H_6	9P(28)	2.0	$0.204 \cdot 10^{+0}$	$0.529 \cdot 10^{+0}$	$0.144 \cdot 10^{+0}$	$0.468 \cdot 10^{+0}$	$0.423 \cdot 10^{+0}$
SO_2	9R(30)	0.11	$0.309 \cdot 10^{+1}$	$0.712 \cdot 10^{+1}$	$0.208 \cdot 10^{+1}$	$0.610 \cdot 10^{+1}$	$0.770 \cdot 10^{+1}$
SF_6	9R(30)	563.5	$0.603 \cdot 10^{-3}$	$0.139 \cdot 10^{-2}$	$0.405 \cdot 10^{-3}$	$0.119 \cdot 10^{-2}$	$0.150 \cdot 10^{-2}$

*The values of ρ_{min}^e were obtained using $\beta^* = \beta + \alpha_a$, where α_a is the aerosol extinction coefficient, taken from Ref. 18.

TABLE V. The limiting detectable concentrations of gases compared with the data of Ref. 9, $\delta_y = \delta_\eta = 5\%, \delta_\rho = 10\%$, $\beta = \beta_b$.

The gas	The transition	The wavelength μm	$K,$ $cm^{-1}atm^{-1}$ of Ref. 9	ρ_{min}^p (R = 1%), ppb		ρ_{min}^p (R = 5%), ppb		ρ_{min}^e, ppb of Ref. 9
				$\beta_b = 0.001$	$\beta_b = 0.003$	$\beta_b = 0.001$	$\beta_b = 0.003$	
C_2H_4	10P(14)	10.532	32.6	0.15	0.44	0.08	0.25	0.7
H_2O	10R(20)	10.246	$7.96 \cdot 10^{-4}$	$6.05 \cdot 10^3$	$1.82 \cdot 10^4$	$3.50 \cdot 10^3$	$1.07 \cdot 10^4$	$2.0 \cdot 10^4$
C_3H_6	9P(22)	9.569	7.54	0.64	1.92	0.36	1.11	2.7
C_3H_3Cl	10P(22)	10.611	7.29	0.66	1.98	0.38	1.14	2.6
C_6H_6	9P(30)	9.639	1.81	2.66	7.99	1.53	4.61	10.0
C_7H_8	9P(36)	9.695	1.13	4.26	12.8	2.45	7.38	20.0
CH_3OH	9P(34)	9.676	18.1	0.27	0.79	0.15	0.46	1.4
C_2H_5OH	9R(26)	9.239	3.77	1.18	3.83	0.73	2.21	6.0

The limiting detectable concentrations of gases, determined from the relation ρ_{min}^e (Ref. 9) $= \beta_b/K$ where ρ_{min}^e are the experimental values, are presented in Ref. 9; β_b is the background absorption coefficient. The values of β_b, measured by Mayer and Sigrist,[9] for synthetic air $(N_2 + O_2)$ were equal to

$(1-3) \cdot 10^{-8}$ cm^{-1}. Our values of ρ_{min}^p are compared in Table V with the data of Ref. 9. The signals were calculated for the following parameters: $M_\eta/y_0 = 3.5$ V · cm/Wt (Ref. 9), $\beta = \beta_b = 10^{-3}$, $3 \cdot 10^{-3}$ km^{-1}. Table V also gives the absorption coefficients K from Ref. 9, which were used to cal-

culate ρ^p_{min}. Analysis of the data in Table V shows that the limiting possibilities of the optoacoustic system are indeed higher (even for the high-efficiency mode of detection $R = 1\%$ $\rho^p_{min} < \rho_{min}$ (Ref. 9)).

CONCLUSIONS

The proposed algorithm makes it possible to select wavelengths that are informative for the purposes of optoacoustic gas analysis. The results of modeling are consistent with the physical nature of the problem being solved: the spectral sections with the highest absorption coefficients are most informative in the BAD method of measuring gas concentrations. However choosing the wavelength at which the absorption coefficient is highest is still not a sufficient condition for detecting a gas in the experiment. The algorithm permits determining the experimental conditions under which the gas can be detected: the concentration of the "background" gases 0, the accuracy of the measurement of the signals σ_y, and the range of the detected concentration in the gas being analyzed.

The numerical experiment performed showed that the minimum (with a risk of 5%) detectable absorption coefficient for the gas under study α_j is $\sim 0.3(\beta_{int} + \beta_b)$ for $\delta_y = \delta_\eta = 5\%$, $\delta_a = 10\%$ where β_{int} is the volume absorption coefficient of the "interfering" gases and β_b is the background absorption coefficient.

We thank G.N. Glazov and S.D. Tvorogov for a fruitful discussions at the starting stage of this work and B.G. Ageev for a consultation concerning the method for measuring gas concentrations with the help of an optoacoustic detector.

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