# DETECTION OF GASES WITH THE HELP OF AN OPTOACOUSTIC GAS ANALYZER

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*Two algorithms for detecting the gases have been constructed for an optoacoustic (OA) gas analyzer. The first algorithm is based on the Bayesian criterion of minimum average risk, the second — on the Neumann–Pearson criterion. The results of processing of the signal of the OA gas analyzer based on a $CO_2$ laser are given in the paper. The results are in a good agreement with the experimental data.*

## STATEMENT OF THE PROBLEM

Interpretation of the data obtained from the gas analyzer measurements calls for the construction of the proper mathematical algorithms. Depending on the posed problem the algorithms can be intended for both quantitative analysis of a gas mixture (the measurement problem) and quantitative analysis when the measured optical parameters of the gas mixture volume being studied are used for determining the presence of a certain gas in the mixture or the deviation of its concentration from a certain fixed level (the detection problem). The detection problem is closely associated with the accuracy characteristics of a measurement equipment as well as to the degree of overlap of the absorption lines (bands) of the gas being studied with that of the other gases. If the signal–to–noise ratio is low and the effect of the interfering gases is strong, the relative errors in the estimate of the gas concentration from the optical measurements can reach more than 100%. In this case preference must be given not to the quantitative analysis of a gas mixture but to the determination of the probability of the presence or absence of gases in the mixture.

In this paper we deal with the processing algorithms for the problems of gas detection with the help of an optoacoustic gas analyzer. To this end, two criteria are employed. The first is the Bayesian criterion of the minimum average risk, the second is the Neumann–Pearson criterion. The results of processing of the signals of the OA gas analyzer based on a $CO_2$ laser are given in the paper.

We will study a gas mixture only one component of which is to be analyzed. The other gases in this mixture are considered to be background. When a quasimonochromatic radiation source is used the relation between the measured signal and the concentration of the gas being studied $\rho$, is given by the formula[1]

$$\bar{y} = y_0 \eta \, [K\rho + \beta] \,, \tag{1}$$

where $\bar{y}$ is the average value of the measured OA signal, $y_0$ is the radiation power at the input into the cell of the optoacoustic detector (OAD), $\eta$ is the OAD sensitivity, $K$ is the coefficient of absorption per unit concentration of gas, $\beta$ is the volume coefficient of the absorption by the other gases of the mixture and of the nonselective absorption by walls and windows of the OA cell $\beta_{bg}$.

The detection problem reduces to checking the statistical hypothesis $H_1$, based on the measured parameter $y$, that the information parameter $\rho$ belongs to the class of states $X_1$ as opposed to the alternative $H_2$ according to which $\rho$ belongs to the class $X_2$ (see Ref. 2).

Let the classes of the states $X_1$ and $X_2$ are fixed by the conditional probability densities $\tilde{P}(y|H_i) = \tilde{P}(y|\rho \in X_i)$ averaged over the interfering parameters $y_0$, $\eta$, and $\beta$.

The Bayes decision rule minimizing the average risk has the form[2]

$$l(y) \gtrless \Lambda \,, \rightarrow \rho \in \begin{cases} X_2 \\ X_1, \end{cases} \tag{2}$$

with the threshold value $\Lambda$ being equal to

$$\Lambda = \ln\left[\frac{q(\Pi_{12} - \Pi_{11})}{p(\Pi_{21} - \Pi_{22})}\right], \tag{3}$$

where $l(y)$ is the logarithm of likelihood ratio

$$l(y) = \ln\left[\frac{\tilde{P}(y|H_2)}{\tilde{P}(y|H_1)}\right], \tag{4}$$

$q$ and $p = 1 - q$ are the *a priori* probabilities of the fact that the independent parameter $\rho$ belongs to the mutually complementary regions $X_1$ and $X_2$, $\Pi_{ij}$ are the elements of the matrix of losses.

The quality of the decision rule is determined by the average risk $R$ (see Ref. 2):

$$R = q\Pi_{11} + p\Pi_{21} + q(\Pi_{12} - \Pi_{11})\varepsilon_1 - p(\Pi_{21} - \Pi_{22})(1 - \varepsilon_2). \tag{5}$$

The Neumann–Pearson detection rule has the same form as Eq. (2), the detector threshold value $\Lambda$ in this case is found from the condition

$$\varepsilon_1 = \int_{\Lambda}^{\infty} \tilde{P}(l|H_1) \, dl = \varepsilon_0, \tag{6}$$

with a fixed value of $\varepsilon_0$ (see Ref. 2).

The probability of correct detection according to this rule is calculated from the formula

$$P = 1 - \varepsilon_2 = 1 - \int_{-\infty}^{\Lambda} \tilde{P}(l|\rho \in X_2) \, dl \,, \tag{7}$$

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where $P(l|\rho \in X_i) = P(l|H_i)$ are the conditional probability densities of the random value $l$.

## CALCULATION OF THE DETECTION CHARACTERISTICS Λ, *R*, AND *P*

To calculate the logarithm of the likelihood ratio $l(y)$ and the errors of the first and second kind $\varepsilon_1$ and $\varepsilon_2$, we must know the form of the probability distributions $P(y|H_i)$, $P(\eta)$, $P(\beta)$, and $P(y_0)$.

1. We will assume that $P(y|H_i)$ are the normal distributions for both hypotheses with the parameters $M_{y_i}$, $\sigma^2_{y_i}$, in this case $\sigma_{y_1} = \sigma_{y_2} = \sigma_y$.

2. $P(y_0)$ is normal distribution with the parameters $M_0$, $\sigma^2_{y_0}$.

3. $P(\eta)$ and $P(\beta)$ are the δ–functions.

When the condition $M_0/\sqrt{2}\sigma_{y_0} \geq 3$ is satisfied and $\sigma_y$ is assumed to be independent of $\rho$ the conditional probability densities $\tilde{P}(y|H_i)$ averaged over the parameters $y_0$, $\eta$, and $\beta$ will be the normal distributions with the parameters $(M_i, \sigma_i^2)$ being equal to

$$M_1 = M_0\eta\,(K\rho_1 + \beta)\,;\ \sigma_1 = \sqrt{\sigma_y^2 + s_{y_0}^2\,\eta\,(K\rho_1 + \beta)^2}\,;$$

$$M_2 = M_0\eta\,(K\rho_2 + \beta)\,;\ \ \sigma_2 = \sqrt{\sigma_y^2 + \sigma_{y_0}^2\,\eta\,(K\rho_2 + \beta)^2}\,; \quad (8)$$

where $\rho_1$ and $\rho_2$ are the gas concentrations corresponding to the hypothesis $H_1$ and $H_2$.

The elements of the matrix of losses and the *a priori* probabilities are assumed to be $\Pi_{11} = \Pi_{22} = 0$; $\Pi_{12} = \Pi_{21} = 1$; $p = q = 0.5$.

For the normal distributions $\tilde{P}(y|H_i)$ and the given values of $q$, $p$, and $\Pi_{ij}$ it is possible to derive the following relations for calculating the threshold value Λ, the errors $\varepsilon_1$ and $\varepsilon_2$, the risk $R$, and the probability of correct detection $P$.

*A) The Bayesian detection criterion*

$$\Lambda^B = 0\,, \quad (9)$$

$$\varepsilon_1 = \frac{1}{2}\left[1 - \Phi\left(g_1^B\right)\right], \quad (10)$$

$$\varepsilon_2 = \frac{1}{2}\left[1 - \Phi\left(g_2^B\right)\right], \quad (11)$$

$$R = \frac{1}{2}[\varepsilon_1 + \varepsilon_2], \quad (12)$$

where

$$\Phi(g) = \frac{2}{\sqrt{\pi}}\int_0^g \exp(-t^2)\,dt\,.$$

$$g_1^B = \frac{(-1)^{n+1}\left(\sqrt{|\Lambda^B + d|} - |\tilde{M}_1|\right)}{\sqrt{2}\,\tilde{\sigma}_1}\,;$$

$$g_2^B = \frac{(-1)^{n+1}\left(|\tilde{M}_2| - \sqrt{|\Lambda^B + d|}\right)}{\sqrt{2}\,\tilde{\sigma}_2}\,. \quad (13)$$

Depending on the relation between $\rho_1$ and $\rho_2$ the parameter $n$ takes the following values: a) $\rho_2 > \rho_1$, $n = 1$ and b) $\rho_2 < \rho_1$, $n = 2$.

In formula (13) the parameters $\tilde{M}_i$, $\tilde{\sigma}_i^2$ and $d$, where $i = 1, 2$, are related to the parameters $M_i$ and $\sigma_i^2$ via the formulas

$$\tilde{M}_1 = \frac{1}{\sqrt{2}}\frac{M_2 - M_1}{\sqrt{|\sigma_2^2 - \sigma_1^2|}}\frac{\sigma_1}{\sigma_2}\,;\ \tilde{M}_2 = \frac{1}{\sqrt{2}}\frac{M_2 - M_1}{\sqrt{|\sigma_2^2 - \sigma_1^2|}}\frac{\sigma_2}{\sigma_1}\,, \quad (14)$$

$$\tilde{\sigma}_1^2 = \frac{|\sigma_2^2 - \sigma_1^2|}{2\sigma_2^2}\,;\ \tilde{\sigma}_2^2 = \frac{|\sigma_2^2 - \sigma_1^2|}{2\sigma_1^2}\,, \quad (15)$$

$$d = \frac{(M_2 - M_1)^2}{2(\sigma_2^2 - \sigma_1^2)} + \ln\frac{\sigma_2}{\sigma_1}\,. \quad (16)$$

Formulas (10)–(13) are valid when the following conditions are satisfied:

a) $\dfrac{M_0^2}{12\sigma_{y_0}^2} \geq \dfrac{|M_1|}{\sqrt{2}\sigma_1} \geq 3;\ \dfrac{|M_2|}{\sqrt{2}\sigma_2} \geq 3;$ for $\sigma_2 > \sigma_1$,

b) $\dfrac{M_0^2}{12\sigma_{y_0}^2} \geq \dfrac{|M_2|}{\sqrt{2}\sigma_1} \geq 3;\ \dfrac{|M_1|}{\sqrt{2}\sigma_2} \geq 3;$ for $\sigma_2 < \sigma_1$.

*B) The Neumann––Pearson criterion*

$$\Lambda^{N-P} = -d + (-1)^{n+1} \times$$

$$\times\left[\,|\tilde{M}_1| + (-1)^{n+1}\sqrt{2}\,\Phi^{-1}(1 - 2\varepsilon_0)\right]^2, \quad (17)$$

a) $\rho_2 > \rho_1$, $n = 1$; b) $\rho_2 < \rho_1$, $n = 2$.

The probability of correct detection for both cases is calculated from the formula

$$P = 1 - \varepsilon_2^{N-P} = \frac{1}{2}\left[1 + \Phi\left(g_2^{N-P}\right)\right], \quad (18)$$

where $g_2^{N-P}$ is determined by relation (13) for $g_2^B$ in which $\Lambda^B$ must be replaced by $\Lambda^{N-P}$.

## RESULTS OF PROCESSING OF THE OA SIGNALS

The detection algorithms were tested with the use of the experimental data obtained by Meyer and Sigrist.[3] The authors have developed an optoacoustic system based on a $CO_2$ laser for monitoring the atmospheric gaseous pollutants. The signals were recorded using a resonance OA cell.

We will now give the result of processing of the OA signals initiated by a $CO_2$ laser radiation on two transitions: 10P(14) with $\nu_l = 949.479$ and 10P(20) with $\nu_l = 944.194$ cm$^{-1}$.

The first transition is used for detecting ethylene, the second is for carbon dioxide. In detecting $C_2H_4$ the background gases are $H_2O$ and $CO_2$, the effect of the other gases can be neglected. The relation between the measured signal and the ethylene concentration is given by formula (1). The coefficient β for the OA system described in Ref. 3 has the form

$$\beta = -\left(\frac{\nu_{N_2}}{\nu_l} - 1\right) K_{CO_2} \rho_{CO_2}^{bg} + K_{H_2O} \rho_{H_2O}^{bg} + \\ + \alpha_K\left(\rho_{H_2O}^{bg}\right) + \beta_{bg}, \qquad (19)$$

where $\nu_{N_2}$ is the frequency of the first vibrational mode of $N_2$ equal to 2330 $cm^{-1}$, $\nu_l$ is the laser radiation frequency, $K_i$ and $\rho_i^{bg}$ are the selective absorption coefficients and concentration of the background gases ($CO_2$ and $H_2O$), $\alpha_K(\rho_{H_2O}^{bg})$ is the coefficient of the $H_2O$ continuous absorption calculated from the empirical formula given in Ref. 4, $\beta_{bg}$ is the coefficient of the background signal absorption.

In detecting $CO_2$ the background gases are $C_2H_4$ and $H_2O$. In this case the measured signal of the OA system[3] is related to the $CO_2$ concentration via the formula

$$\bar{\nu} = y_0 \eta \left[ -\left(\frac{\nu_{N_2}}{\nu_l} - 1\right) K_{CO_2} \rho_{CO_2} + \beta \right], \qquad (20)$$

where β is determined from relation (19) in which $K_{C_2H_4}\rho_{C_2H_4}^{bg}$ stands for the first term.

The formulas for the parameters $M_i$ and $\sigma_i$, where $i$ = 1, 2, derived for relation (20) differ from Eq. (18) in that the term $-(\nu_{N_2}/\nu_l - 1)K\rho_i$ appears in place of $K\rho_i$. Therefore, depending on the values $\rho_1$ and $\rho_2$ even with $\rho_2 > \rho_1$ the relations between $\sigma_1$ and $\sigma_2$ for $CO_2$ can be different, that is, the following situations can be observed: a) $\sigma_2 > \sigma_1$, b) $\sigma_2 < \sigma_1$, and c) $\sigma_2 = \sigma_1$. For the two first situations the formulas for calculating the detection characteristics Λ, $R$, and $P$ have already been derived here (see Eqs. (9)–(17)). For the case (c), in which $\sigma_2 = \sigma_1$, the differences will occur only in the relations for $g_1^B$, $g_2^B$, and $\Lambda^{N-P}$. Given below are the formulas for calculating $g_i^B$, where $i$ = 1, 2, and $\Lambda^{N-P}$, when $\sigma_1 = \sigma_2 = \sigma$

$$g_1^B = \frac{E + L^B}{2\sqrt{E}}; \quad g_2^B = \frac{E - L^B}{2\sqrt{E}}; \qquad (21)$$

where

$$E = \frac{(M_2 - M_1)^2}{2\sigma^2}. \qquad (22)$$

In signal processing we used the following parameters of the OA system: $\eta/M_0$ = 3.5 V·cm/W, $M_0$ = 1 W, $\sigma_{y_0} = 0.05\, M_0$, $\sigma_y$ = 0.05 μV, and $\beta_{bg} = 3\cdot10^{-8}$ $cm^{-1}$ (see Ref. 3).

Table I lists the absorption coefficients $K_{H_2O}$, $K_{CO_2}$, and $K_{C_2H_4}$. The coefficients $K_{H_2O}$ were calculated from the data published in the Atlas[5]; the coefficients $K_{CO_2}$ and $K_{C_2H_4}$ were borrowed from Ref. 3. The background gas concentrations $\rho^{bg}$ were: $\rho_{CO_2}^{bg}$ = 330 ppmV,[6] $\rho_{C_2H_4}^{bg} = 2\cdot10^{-2}$ ppmV.[3] The background value of $\rho_{H_2O}^{bg}$ was borrowed from the regional model[7] which incorporated a geographic region (Switzerland) of the experiment[3] and for winter conditions $\rho_{H_2O}^{bg}$ = 5.08 g/$m^3$ while the temperature was 2°C. When the hypotheses were checked, the following concentrations in the hypotheses $H_1$ and $H_2$ were taken for ethylene: $\rho_1$ = 5 ppbV, $\rho_2$ = 20 ppbV and for $CO_2$ $\rho_1$ = 330 ppbV and $\rho_2$ = 360 ppbV.

*TABLE I. Absorption coefficients,* $atm^{-1}\cdot cm^{-1}$.

| Frequency of transition, $cm^{-1}$ | $K_{H_2O}$ | $K_{CO_2}$, Ref. 3 | $K_{C_2H_4}$, Ref. 3 |
|---|---|---|---|
| 949.479 | $2.443\cdot10^{-6}$ | $3.20\cdot10^{-3}$ | 32.7 |
| 944.194 | $2.322\cdot10^{-6}$ | $4.00\cdot10^{-3}$ | 1.64 |

The results of processing of the OA signals are listed in Tables II and III. The measurements published in Ref. 3 were made on February 4, 1986 during the day near a motor way.

As follows from Table II, only in morning and evening the ethylene content fits the hypothesis $H_1$. During the rest of time both algorithms fit the hypothesis $H_2$. This can be explained by the increased number of motorcars during a day. The value of the risk $R < 10^{-5}$, that is, close to zero while $P$ equals to unity to an accuracy of up to $10^{-4}$. Such a small value of $R$ is indicative of the fact that the states $X_1$ and $X_1$ corresponding to the concentrations $\rho_1$ = 5 ppbV and $\rho_2$ = 20 ppbV are classified sufficiently reliably. The last column in Table II shows the measurements of the ethylene content obtained by Meyer and Sigrist[3] which verify the efficiency of the detection algorithms. It can be seen from Table III that during the day the $CO_2$ content fits the hypothesis $H_1$ and $\rho_1$ = 330 ppbV, the value of the risk in this case is equal to 11% and the probability of correct detection according to the Neumann–Pearson criterion is 80%.

*TABLE II. Results of processing of the* OA *signals in* $C_2H_4$ *detection* $H_1$: $\rho_1$ = 5 ppbV and $H_2$: $\rho_2$ = 20 ppbV.

| The number of the hypothesis | Local time, hours | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| | OA signal, Ref. 3, μV/W | | | | | | | | | | | | | | | | |
| | –1.50 | 0.75 | 2.25 | 0.25 | –0.75 | –0.25 | –0.25 | –0.30 | 0.50 | 1.50 | 1.60 | 3.40 | 4.00 | 1.75 | –0.20 | –2.00 | –2.00 |
| $H_i^B$, $i$ = 1, 2 $R$ = 0.0 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 |
| $H_i^{N-P}$, $i$ = 1, 2 $\varepsilon_0$ = 0.05, $P$ = 1.0 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 |
| Concentration, Ref. 3 $\rho_{C_2H_4}$, ppbV | 11 | 30 | 45 | 27 | 18 | 22 | 23 | 21 | 29 | 37 | 38 | 55 | 60 | 40 | 23 | 7 | 8 |

*TABLE III. Results of processing of the* OA *signals in* $CO_2$ *detection* $H_1$: $\rho_1$ = 330 ppmV and $H_2$: $\rho_2$ = 360 ppmV.

| The number of the hypothesis | Local time, hours | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| | OA signal, Ref. 3, μV/W | | | | | | | | | | | | | | | | |
| | –3.10 | –3.40 | –3.3 | –3.75 | –3.50 | –3.20 | –3.50 | –3.30 | –3.50 | –3.70 | –3.50 | –3.40 | –3.50 | –3.30 | –3.30 | –3.20 | –3.30 |
| $H_i^{B^*}$, $i$ = 1, 2 $R$ = 0.108 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $H_i^{N-P^{**}}$, $i$ = 1, 2 $\varepsilon_0$ = 0.05, $P$ = 0.799 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

*The Bayesian criterion.

**The Neumann–Pearson criterion.

Thus the results of processing of the OA signals allows us to draw two conclusions. First, the comparison with measured concentrations of $C_2H_4$ shows that both detection algorithms can successfully be employed in the problems of gas analysis with the help of an optoacoustic detector. Second, both algorithms indicate that one and the same hypothesis, $H_1$ or $H_2$ , is true, therefore, in further studies it is possible to use only one of these algorithms.

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