

Comparative analysis of the methods of searching spectral measurement channels for a laser photoacoustic gas analyzer

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Algorithms for searching spectral measurement channels for a laser photoacoustic differential absorption gas analyzer intended for quantitative analysis of multicomponent gas mixtures are compared. Advantages and disadvantages of various algorithms are considered. It is shown that our algorithm of searching the spectral measurement channels accounts for major factors affecting operation of a gas analyzer and requires only little computations. Therefore, it is preferable, among others, from the viewpoint of the analysis efficiency and operation rate.

The set of spectral measurement channels (SSMCh) employed in a laser-based photoacoustic gas analyzer considerably affects the measurement accuracy. For multicomponent gas mixtures with overlapping spectra of the components, selecting the SSMCh is too a complicated problem for being solved immediately in making nearly real-time gas analysis. Various criteria are used in selecting SSMCh for analysis of multicomponent mixtures.¹⁻¹⁴ However, not all of them can be used in gas analysis with a laser photoacoustic differential absorption gas analyzer. In this paper, we analyze the criteria of SSMCh selection for analysis of multicomponent gas mixtures.

The problem of SSMCh selection is closely connected with the problem on reconstruction of gas concentrations (because the error in reconstruction of gas concentrations is the most significant indicator of the proper selection of SSMCh). The problem of determining gas concentrations of an n -component gas mixture from measurements with a laser photoacoustic gas analyzer (LPAGA) (in the case that the laser lines are much narrower than that of gas absorption lines) can be reduced to solution of the system of m ($m \geq n$) linear algebraic equations of the following form:

$$\begin{cases} \kappa_{11}N_1 + \kappa_{12}N_2 + \dots + \kappa_{1n}N_n + \beta_1 = y_1 \\ \dots \\ \kappa_{m1}N_1 + \kappa_{m2}N_2 + \dots + \kappa_{mn}N_n + \beta_m = y_m \end{cases}, \quad (1)$$

where κ_{ji} is the absorption coefficient of the i th gas component for the j th spectral channel; N_i is the sought concentration of the i th component; β_j and y_j are the coefficient of nonselective absorption and the reduced signal measured in the j th spectral channel.

Measurements by the differential absorption (DA) method require $m = 2n$ spectral channels to be used, which are selected by pairs (for every gas) located closely to each other to exclude the effect of

nonselective absorption that weakly depends on the wavelength. Subtracting equations in the system (1) by pairs, we obtain the following system of equations:

$$\begin{cases} \Delta\kappa_{11}N_1 + \Delta\kappa_{12}N_2 + \dots + \Delta\kappa_{1n}N_n = \tilde{y}_1 \\ \dots \\ \Delta\kappa_{n1}N_1 + \Delta\kappa_{n2}N_2 + \dots + \Delta\kappa_{nn}N_n = \tilde{y}_n \end{cases}, \quad (2)$$

where $\Delta\kappa_{ji} = \kappa_{(2j-1)i} - \kappa_{(2j)i}$; $\tilde{y}_j = y_{2j-1} - y_{2j}$.

Consider now the criteria of SSMCh selection for the problem of multicomponent gas analysis.

Criteria based on optimization of gas analyzer characteristics

Characteristics of gas analyzers have earlier been generalized in Ref. 5. As a partial-content sensitivity γ_{ji} , it is proposed to use the derivative of the signal y_j in the j th channel with respect to the concentration of the i th mixture component⁵: $\gamma_{ji} = \partial y_j / \partial N_i$.

For the system of equations (1), γ_{ji} is equal to the absorption coefficient κ_{ji} . The total sensitivity H is suggested to be determined as a determinant of the matrix of partial-content sensitivity values.^{5,7,8} For the systems (1) and (2), the value of H is correspondingly equal to the determinant of the matrix of absorption coefficients.

As a measure of selectivity (characterizing the possibility of independent determination of mixture components), we propose to use quantity Ξ defined in Ref. 5 as follows:

$$\Xi = \min_{i=1\dots n} |\kappa_{ii}| \left(\sum_{k=1}^n |\kappa_{ik}| - |\kappa_{ii}| \right)^{-1} - 1. \quad (3)$$

Optimization of these characteristics can be used as a basis for the SSMCh search.⁵

Criteria based on analysis of the Z matrix

Some criteria for the SSMCh search based on analysis of the matrix Z have been described in Ref. 3. The matrix Z is formed in the least-squares method for calculation of the vector of unknown concentrations:

$$\mathbf{N} = Z\mathbf{y}, \quad (4)$$

where \mathbf{y} is the vector of reduced signals (the right-hand side of the system (1)); $Z = (K^T K)^{-1} K^T$; K is the matrix of the absorption coefficients entering into the left-hand side of the system (1).

To minimize the variance and the maximum error in determination of the i th mixture component, one has to minimize the corresponding functions D_i and Φ_i (Refs. 1 and 3) at the set of all possible SSMCh:

$$D_i = \sum_{j=1}^m (z_j^i)^2; \quad \Phi_i = \sum_{j=1}^m |z_j^i|, \quad (5)$$

where z_j^i is the element of the matrix Z at the intersection of the i th row and the j th column.

The error in all components determined is minimized through minimization of the functions D and Φ (D - and Φ -criteria)³:

$$D = \sum_{i=1}^n D_i; \quad \Phi = \sum_{i=1}^n \Phi_i. \quad (6)$$

Criterion using the condition number

Conditionality of systems of linear algebraic equations (SLAE) for an optimal SSMCh selection has been considered in Ref. 15. The error in solution of gas analysis SLAE (1) at an insufficiently accurate right-hand side (that is, under noisy conditions) is determined by the inequality:

$$\|\mathbf{N}_{\text{ERR}}\| \|\mathbf{N}\|^{-1} \leq \text{cond}(K) \|\mathbf{y}_{\text{ERR}}\| \|\mathbf{y}\|^{-1}, \quad (7)$$

where

$$\text{cond}(K) = \|K\|_M \|K^{-1}\|_M; \quad (8)$$

$\|\bullet\|$ is some vector norm; $\|\bullet\|_M$ is some matrix norm; K is the matrix of absorption coefficients; \mathbf{y}_{ERR} is the error vector of the right-hand side of the system (1); \mathbf{N}_{ERR} is the error vector of solution; $\text{cond}(K)$ is the condition number of the matrix K .

Minimizing (on the set of all possible SSMCh) the expression

$$\text{cond}(K) \|\mathbf{y}_{\text{ERR}}\| \|\mathbf{y}\|^{-1}, \quad (9)$$

one can minimize the maximum error of reconstruction of gas concentrations.

Criterion using maximization of the information distance

Algorithms for SSMCh selection based on the Bayes approach can be found in Refs. 12–14. For SSMCh selection, it is proposed to maximize the information distance L in the space of states of the gas object under study¹⁴:

$$L = \sqrt{\sum_{i,j} (N_2 - N_1)_i (R^T V^{-1} R)_{ij} (N_2 - N_1)_j}, \quad (10)$$

where $(N_2 - N_1)_i$ is the range of variability of the i th component concentration; R is an $n \times n$ matrix, $R_{ij} = W_0^j \eta \kappa_{ji}$; W_0^j is the radiation power at the cell entrance for the j th spectral channel; η is the calibration constant; V is the diagonal matrix with the following elements:

$$\sigma_j^2 = \sigma_U^2(j) + (\delta_W^2 + \delta_\eta^2) \eta^2 (W_0^j)^2 \left(\sum_i \kappa_{ji} N_{2i} + \beta_j \right)^2;$$

$\sigma_U^2(j)$ is the variance of measurement error of an acoustic signal in the j th channel; $\delta_{W,\eta}$ are the relative measurement errors in W_0^j and η .

Criterion based on analysis of the variance-covariance matrix

The variance-covariance matrix $V(\mathbf{N})$ connected with the solution vector \mathbf{N} of the system of nonlinear equations of gas analysis is defined as follows⁶:

$$V(\mathbf{N}) = (K^T K)^{-1} \sigma_y^2, \quad (11)$$

where σ_y^2 is the variance of measurement error of \mathbf{y} (the variance of the measurement error is assumed to be the same for all spectral channels).

As a criterion for SSMCh selection, it is proposed⁶ to use minimization of the sum of diagonal elements of the matrix $V(\mathbf{N})$ (they determine variances of the components of the solution vector \mathbf{N} obtained by the least-squares method):

$$\min \sum_i V(\mathbf{N})_{ii}. \quad (12)$$

Criterion based on the coefficient of information content

In Refs. 3 and 9, it was proposed to select SSMCh by maximizing the coefficient r_i^j determining the measure of information about the i th gas component contained in the j th spectral channel:

$$r_i^j = \kappa_{ji} \bar{N}_i \left(\sum_{p=1}^n \kappa_{jp} \bar{N}_p \right)^{-1}, \quad (13)$$

where \bar{N}_i is the mean concentration of the i th component allowed by the problem conditions (expected based on the *a priori* data).

Criterion of $\cos \alpha_i^j$ for search of a set of spectral measurement channels

In Refs. 11 and 16, it was proposed to search the SSMCh by maximizing the criterion of $\cos \alpha_i^j$:

$$\cos \alpha_i^j = \kappa_{ji}(\bar{N}_i) \left(\sum_{p=1}^n (\kappa_{jp} \bar{N}_p)^2 \right)^{-1/2}. \quad (14)$$

Consider now the possibility of using the criteria described above for a LPAGA operating in the DA mode. For a LPAGA, it is possible to construct the criteria for SSMCh selection based on maximization of different gas analyzer characteristics. However, such criteria do not meet practical needs, because they are only indirectly connected with the most important characteristic of LPAGA operation, namely, the error of reconstruction of gas concentrations.

The D and Φ criteria [Eqs. (6)] for the SSMCh search can be used for a LPAGA operating in the DA mode, but they should be modified as follows:

$$D = \sum_{i=1}^n \sum_{j=1}^n (\Delta z_j^i)^2 \sigma_{\Delta z_j}^2; \quad \Phi = \sum_{i=1}^n \sum_{j=1}^n |\Delta z_j^i| \Delta(\tilde{y}_j), \quad (15)$$

where Δz_j^i is the element of the i th row and j th column of the matrix $\Delta Z = \Delta K^{-1}$; $\sigma_{\Delta z_j}^2$ is the variance of measurements of the reduced signal difference in the j th pair of spectral channels; $\Delta(\tilde{y}_j)$ is the measurement error in the reduced signal difference in the j th pair of spectral channels.

The criterion based on the condition number of the matrix of SLAE coefficients for a LPAGA operating in the DA mode can be written as follows:

$$\text{cond}(\Delta K) \|\tilde{\mathbf{y}}_{\text{ERR}}\| \|\tilde{\mathbf{y}}\|^{-1}. \quad (16)$$

Using this criterion, we can account for the inaccuracy in absorption coefficients, source line intensity, and noise level in the measurement channels.

A criterion of maximization of the information distance is promising, since it accounts for the intensity of spectral lines of the source, errors in the information signal, radiation power, and calibration constants. However, the criterion given by Eq. (10) should be modified for analysis of multicomponent mixtures with overlapping spectra.

The criterion (12) allows minimization of the variance of the concentration vector obtained by the least-squares method and, in fact, it is close to the D - and Φ -criteria.

The use of the criteria of maximization of the information content coefficients (13) and cosines (14) involves complicated *a priori* estimation of the concentration values.

The analysis shows that both the D - and Φ -criteria (15) and criterion (16) can be used for the SSMCh search for a LPAGA operating in the DA mode. However, they require consideration of all combinations of spectral channels, what calls for cumbersome computations. The use of a genetic algorithm (GA)¹⁷ is promising, but GA is computationally expensive as well (although less expensive than consideration of all combinations).

Thus, the SSMCh selection method for real-time gas analysis should not require bulky computations. Below we describe a version of such a heuristic method. It does not require consideration of all possible SSMCh and accounts for the main factors (for every pair of spectral channels the difference between the absorption coefficients of a corresponding gas is maximum; the effect of other gases and the spectral dependence of the laser power are taken into account). The method consists in the following:

1. At the first stage, the search for possible pairs of spectral channels is performed for each gas. For each possible spectral channel with the number j_{on} (corresponding to the maximum absorption by the analyzed gas component), the second spectral channel j_{off} (corresponding to the minimum absorption by the analyzed gas component) is selected from some limited spectral region so that the cost parameter F

$$F(i, j_{\text{on}}, j_{\text{off}}) = (1-b) \left[w_0^{j_{\text{on}}} \kappa_{j_{\text{on}}i} - \kappa_{j_{\text{off}}i} / w_0^{j_{\text{off}}} \right] - b \left\{ \sum_{l \neq i}^n [\kappa_{j_{\text{on}}l} + \kappa_{j_{\text{off}}l}] + \sum_{l \neq i}^n |\kappa_{j_{\text{on}}l} - \kappa_{j_{\text{off}}l}| \right\}, \quad (17)$$

is maximum. Here i is the number of the spectral component analyzed; n is the number of components in the gas mixture; j_{on} and j_{off} are the numbers of wavelengths of a pair of spectral channels with high and low absorption coefficients of the i th gas component; w_0^j is the relative (normalized to the laser radiation power maximum over all laser lines) power of laser radiation at the cell entrance for the j th spectral channel; b is the empirical coefficient (determined from the results of previous tests) accounting for the effect of other gases in the mixture (the coefficient b is selected from the range of 0–1, and $b = 0$ corresponds to the case that the effect of other gases is completely ignored).

2. The pairs are ranked separately for each gas in accordance with the cost parameter F .

3. Such a set of wavelength pairs is selected, for which the parameter F is maximum under condition that wavelengths in the set of spectral channels are used only once.

The first term in Eq. (17) has the form

$$(1 - b) (\omega_0^{j_{on}} \kappa_{j_{on}i} - \kappa_{j_{off}i} / \omega_0^{j_{off}}).$$

Maximization of this term involves, first, maximization of the absorption coefficient of the *i*th analyzed gas at the line *j_{on}* and the laser power at this line (for maximization of the term $\omega_0^{j_{on}} \kappa_{j_{on}i}$) and, second, minimization of the absorption index of the *j*th analyzed gas at the line *j_{off}* along with maximization of the laser power at this line (for minimizing the term $\kappa_{j_{off}i} / \omega_0^{j_{off}}$). The laser power should be maximum both for the *on* and *off* lines to decrease the relative measurement error of the reduced signal against the background of additive noise. Both of the terms are measured in the units of absorption, because ω_0^j is the relative power.

The second term in Eq. (17) that accounts for the effect of other gases on the measured results at the lines *j_{on}* and *j_{off}* has the form

$$-b \left\{ \sum_{l \neq i}^n [\kappa_{j_{on}l} + \kappa_{j_{off}l}] + \sum_{l \neq i}^n |\kappa_{j_{on}l} - \kappa_{j_{off}l}| \right\}.$$

To minimize this negative term, one should minimize the coefficients of other gases and the differences of the absorption coefficients of other gases at the lines *j_{on}* and *j_{off}*.

This algorithm involves a little computation even for a multi-dimensional problem, because the parameter *F* is calculated not for the all possible wavelengths, but separately for each pair of spectral channels.

The methods based on Eq. (17) and criteria (15) and (16) were compared for a LPAGA operating in the DA mode using mathematical simulation for various gas

mixtures. For the criteria (15) and (16) the search was performed with the use of GA.

Different methods of spectral channel selection were compared from the viewpoint of two criteria:

(1) errors in reconstructed gas concentrations for selected spectral channels (at a given noise level);

2) computational power needed that is characterized by the time of the search of the set of spectral channels.

Voluminous mathematical simulation has been conducted for various gas mixtures in order to assess our method and known methods of spectral channel selection from the standpoint of these criteria. Some results of mathematical simulations are given below in this paper.

Below we present the results obtained by simulation for an eight-component mixture: ammonia – chloroprene – ethyl acrylate – ethylene – hydrazine – methanol – monomethylhydrazine (MMH) – nonsymmetric dimethylhydrazine (NDMH). Figure 1 depicts the absorption spectra of the gas components of the mixture analyzed.

Table 1 presents the values of criteria of optimal search for the SSMCh based on these criteria. (The first three criteria were modified so that the optimization problem is reduced to the problem of criterion maximization). For the *D*- and Φ -criteria and the criterion based on the condition number, the computation time was fixed at 10 min. For the method based on Eq. (17), the computation time was not limited and was less than 1 s. It can be seen that the values of the first three criteria are close to each other, and using any of them one can obtain the SSMCh with good values of the criteria. However, for these criteria it is not always possible to obtain a suitable (in the meaning of the optimality criteria) SSMCh for acceptable time. In this sense, the criterion (17) is preferable, because the computation time for it is much shorter.

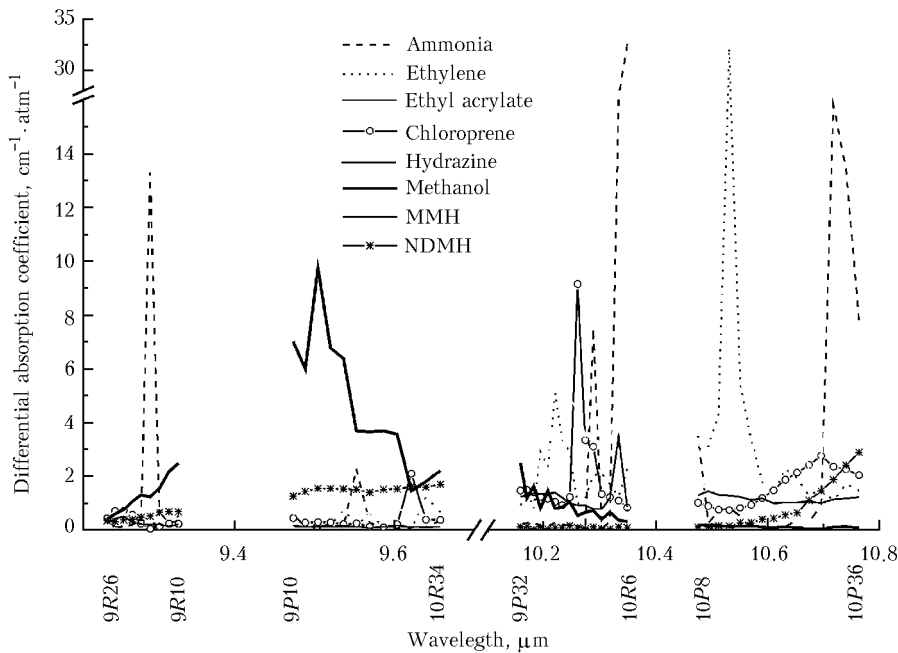


Fig. 1. Absorption spectra of gas components of the 8-component mixture analyzed.

Table 1. Optimality criteria for selected spectral channels

Selection criterion	SSMCh Wavelengths of pairs of spectral channels, μm	Value of the optimality criterion			
		1. Criterion based on condition number	2. Φ -criterion	3. D -criterion	4. Heuristic algorithm
1. Criterion based on condition number	9.294–9.282, 9.317–9.271, 9.536–9.604, 10.289–10.260, 10.476–10.274 10.532–10.591, 10.719–10.764, 10.741–10.675	0.16	0.2	0.71	0.35
2. Φ -criterion	9.294–9.250, 9.504–9.552, 10.260–10.303, 10.334–10.289, 10.349–10.318, 10.532–10.476, 10.571–10.611, 10.719–10.764	0.12	0.22	0.47	1.29
3. D -criterion	9.282–9.250, 9.504–9.552, 10.247–10.260, 10.334–10.289, 10.349–10.318, 10.611–10.551, 10.741–10.696, 10.719–10.764	0.15	0.20	0.72	0.84
4. Heuristic algorithm	9.294–9.261, 9.305–9.250, 9.504–9.552, 10.260–10.233, 10.334–10.303 10.532–10.591, 10.696–10.632, 10.719–10.675	0.14	0.19	0.55	3.27

The computational times presented [10 min for the D - and Φ -criteria and the criterion based on the condition number and 1 s for our method based on Eq. (17)], first, characterize not only computational algorithms, but also the capabilities of the methods for selection of spectral channels (our method, in contrast to other criteria analyzed, does not require consideration of all possible sets of spectral channels) and, second, it gives only the relation between the absolute computational times for different methods (depending on the type of a computer, low-level computational algorithms, and so on) rather than the times themselves.

Figure 2 shows the relative errors in reconstruction of gas concentrations for different criteria of SSMCh selection (numbers 1–4 correspond to the numbers of the criteria in Table 1). The error was calculated as the absolute value of the difference between the preset and the reconstructed values of the concentration divided by the preset value. The results correspond to the

reconstruction error averaged over 100 measurements. The noise in measurements was set at 2.5% level. The gas concentrations were reconstructed by the method of quasi-solutions using the genetic search algorithm.¹⁸ It can be seen from Fig. 2 that the errors of different methods are rather close.

Table 2 gives the final comparison of the SSMCh selection methods using the considered eight-component mixture as a case study. It can be seen from Table 2 that the needed *a priori* information is qualitatively close for all the methods (relative intensity of laser radiation gives an idea of the radiation errors in different channels). The average (over all gases) errors in reconstruction of the component concentrations have close values (about 15%) for all the methods. However, for the D - and Φ -criteria and the criterion based on the condition number, the needed number of calculations of the goal function (to obtain the optimal SSMCh with consideration of all combinations) achieves $\sim 3 \cdot 10^{12}$.

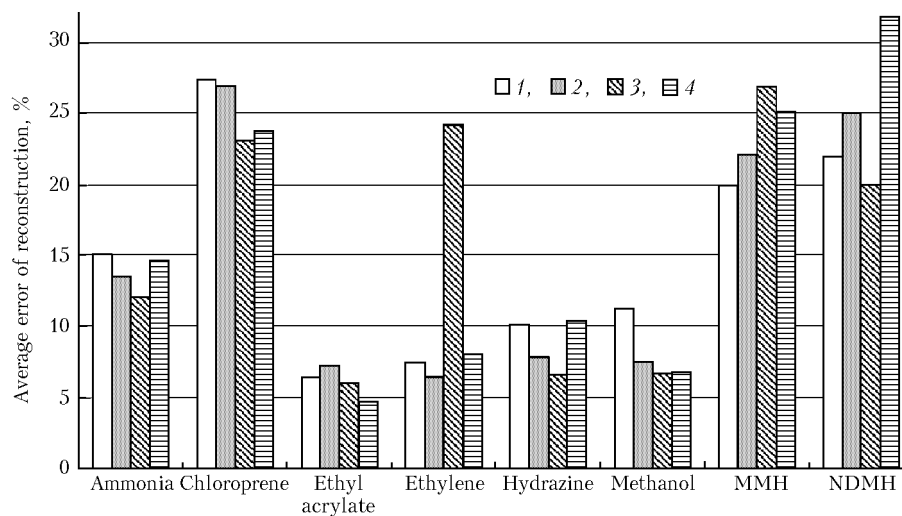
**Fig. 2.** Relative errors of reconstruction of gas concentrations for different criteria of SSMCh selection.

Table 2. Comparison of methods for selection of spectral channels (with an eight-component mixture as a case study)

Selection criterion	<i>A priori</i> information needed	Number of calculations of the goal function	Computation time needed for calculation of the goal function 1120 times, s	Average reconstruction error, %
1. Criterion based on condition number	1. Absorption indices of gases in the analyzed mixture	~ 3 · 10 ¹²	2	15
2. Φ -criterion	2. Error or variance of measurement of reduced signal difference			14.6
3. <i>D</i> -criterion				15.7
4. Heuristic algorithm	1. Absorption indices of gases in the analyzed mixture 2. Relative intensity of laser radiation at entrance into a cell	1120	< 1	15.7

At the same time, the needed number of calculations of the goal function for the heuristic algorithm is nine orders of magnitude smaller. Moreover, the computation time needed for calculation of the goal function in this algorithm is half the time needed by other algorithms (because the goal function in the heuristic algorithm has a simpler form).

Thus, the *D*- and Φ -criteria (15), as well as the criterion (16) based on the condition number, and the method (17) can be used for SSMCh selection for a LPAGA operating in the DA mode. Mathematical simulation for gas mixtures with various qualitative and quantitative composition shows that the use of these criteria gives similar results. However, for real-time gas analysis, the method (17) is more promising from the standpoint of computational expenses.

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