PROCESSING OF SIGNALS FROM A LASER OPTO-ACOUSTIC GAS ANALYZER WHEN STUDYING MULTICOMPONENT GAS MIXTURES

V.I. Kozintsev

Scientific Research Institute of Radioelectronics and Laser Equipment
N.E. Bauman State Technical University, Moscow

Received January 12, 1996

We consider here the algorithms for reconstruction of gas concentrations in multicomponent gas mixtures. The algorithms of signal processing for differential absorption laser photoacoustic experiments derived from regularized solutions of ill-posed inverse problems are described. Results of numerical simulations of reconstruction of concentrations in multicomponent gas mixtures and those for processing signals of laser photoacoustic gas analyzer are presented. It is shown that the use of regularizing procedures for data processing provides for low errors in reconstruction of gas concentration at different methods of selecting regularization parameter. In many cases, selection of regularization parameter on a basis of modified concept of discrepancy gives smoothing of errors which can be caused by the selection of regularization parameter on the basis of the principle of discrepancy or by that of quasioptimal value of the parameter.

Laser gas analysis methods are most promising for remote and local analysis of multicomponent gas mixtures including the problem of air quality control (see Refs. 1–8). In this paper, the procedures of gas component concentrations reconstruction from *in situ* laser measurements, as well as, their comparison with the results of numerical simulations and those from processing signals of laser photoacoustic gas analyzer (LPGA) are described.

The problem on estimation of gas concentration from measurements of LPGA signals is reduced to solution of a set of linear algebraic equations of the following form:

$$\begin{cases} K_a(\lambda_1) + \sum\limits_{j}^{N} C_j\, K_j(\lambda_1) = y(\lambda_1), \\ \dots\dots\dots\dots\dots\dots\dots\dots \\ K_a(\lambda_m) + \sum\limits_{j}^{N} C_j\, K_j(\lambda_m) = y(\lambda_m). \end{cases} \tag{1}$$

Here $y(\lambda_i)$ is the reduced signal measured at the wavelength λ_i; $K_a(\lambda)$ is the coefficient of continuum absorption at the wavelength λ_i; $K_j(\lambda)$ and C_j are the absorption coefficients at the wavelength λ and concentration of the jth gas component, respectively; N is total amount of gas components in the mixture analyzed.

The quantities C_j and $K_a(\lambda_i)$ are unknown in the set of equations (1). Coefficients $K_a(\lambda_i)$ only slightly depend on wavelength. Therefore, it is generally believed that if pairs of spectrally close measurement channels are selected, coefficients K_a for every pair may be considered as constants. In this case of M signals required for gas mixture sounding, $M/2$ signals are necessary to estimate the coefficients K_a.

The problem associated with the solution of Eqs. (1) is that the left-hand sides of equations are always estimated with random measurement errors resulted from instrumental noises and so on. In this case attempts to directly invert Eqs. (1) results in the situation when inverse operator is unstable and small variations in measurement data result in a wide variation in the value sought. In order to correct this situation, one can introduce, into the signal processing procedure, additional *a priori* information about smoothness of the functions sought and construct regularized solutions (see Refs. 6 and 9).

Regularized solution to Eqs. (1) is defined by the following expression (see Refs. 1,6, and 9):

$$(\mathbf{W}^{\mathrm{T}}\, \mathbf{W} + \alpha\, \mathbf{E})\, \mathbf{x}_\alpha = \mathbf{W}^{\mathrm{T}}\, \mathbf{y}. \tag{2}$$

Here α is the parameter of regularization, $\mathbf{x}_\alpha$ is the regularized solution of equations (1);

$$\mathbf{W} = \mathbf{K}_a + \mathbf{K}\, \mathbf{x},$$

$\mathbf{K}$ is the matrix of absorption coefficients of the gas mixture components; $\mathbf{x}$ is the vector of gas concentrations; y is the vector of right-hand sides of the set of equations (1); $\mathbf{K}_a$ is the vector of the continuum absorption coefficients; $\mathbf{E}$ is the unit matrix. The superscript T denotes transposition of a matrix.

0235-6880/96/10 871-04 $02.00

Regularized solution obtained from Eq. (2) is stable to perturbations of the right-hand side of the equation and converges to the exact solution when the perturbations are decreased.

Solution $\mathbf{x}_\alpha$ for the set of equations (2) has the following form:

$$\mathbf{x}_\alpha = (\mathbf{W}^{\mathrm{T}}\,\mathbf{W} + \alpha\,\mathbf{E})^{-1}\,\mathbf{W}^{\mathrm{T}}\,\mathbf{y}. \tag{3}$$

Here $(\mathbf{W}^{\mathrm{T}}\,\mathbf{W} + \alpha\,\mathbf{E})^{-1}$ is the matrix inverse to $\mathbf{W}^{\mathrm{T}}\,\mathbf{W} + \alpha\,\mathbf{E}$.

In the construction of regularized solution, the main difficulty is in selection of the regularization parameter α.

Some methods of selection of α were used to obtain the regularized solution.

Let us assume that instead of the right-hand side of the set of equations (1), $\mathbf{y}$, its value $\tilde{\mathbf{y}}$ satisfying the following condition $\|\mathbf{y} - \tilde{\mathbf{y}}\| \le \delta$ is given. Here $\|\mathbf{y}\|$ is the vector norm.

In the method of estimation of α using the principle of discrepancy, the magnitude of δ represents the deviation of the right-hand side of the set (1) from its exact value. However, δ may be approximately considered as the square root of noise variance of the right-hand side of the set.

Let us introduce the following function (see Refs.6 and 9):

$$r(\alpha) = \rho(\mathbf{W}\,\mathbf{x}_\alpha, \tilde{\mathbf{y}}), \tag{4}$$

Numerical solution of the following equation:

$$r(\alpha) = \delta^2 \tag{5}$$

gives the value of regularization parameter obtained based on the principle of discrepancy.

According to the second method, the quasioptimal regularization parameter was found from the following condition (see Ref.6):

$$\inf_\alpha \|\alpha\,[\mathrm{d}\,\mathbf{x}_\alpha/\mathrm{d}\alpha]\|^2\ . \tag{6}$$

Modification of the method of discrepancy was used as the third way to select α. When tuning over a wide spectral range, measurement noises in different spectral channels may significantly differ. Therefore, individual regularization parameter was used for reconstruction of every gas component concentration. This parameter was found in two steps. At the first step, regularization parameter α_i for every component was evaluated from Eq. (5) written for that spectral channel wherein given component has an absorption peak. At the second step, in the vicinity of obtained α_i value (in the range from α_i to α, the latter was found from Eq. (5) for all spectral channels) the final value of the regularization parameter was deduced from the condition (6).

Also, the method of ratios (see Ref. 6) and a more rigorous expression were used for selection of quasioptimal regularization parameter wherein α is deduced from the following condition (see Ref. 6):

$$\inf_\alpha \sup_y \|\alpha\,[\mathrm{d}\,\mathbf{x}_\alpha/\mathrm{d}\alpha]\|^2\ .$$

Here $\sup_y$ is determined from the set of realizations of the right-hand side of the set (1) (the calculations were performed using 10 realizations). To avoid presenting too many close curves, the calculational results from two methods are not depicted in the figures given below. However, the conclusions drawn from these figures are also true for these methods.

Procedures of LPGA signals processing based on the construction of regularized solution of the set (1) are presented as the package of programs for IBM PC. Absorption cross sections of the gases were calculated using HITRAN-91 data base (see Ref. 10). Concentrations of the gas components resulted from the processing. To check the feasibility of the processing algorithms and to estimate the accuracy of reconstructing component concentrations, numerical simulations and processing of true LPGA signals were carried out.

As a rule, results obtained from actual signals and by numerical simulations indicate that errors in concentration reconstruction for 2-, 3-, and 4-component mixtures are small and the regularization procedures do not improve the accuracy. Minor increase of the accuracy is found for a 5-component mixture, while for 6- (and more) component mixtures the latter increases considerably when the regularization procedures are used.

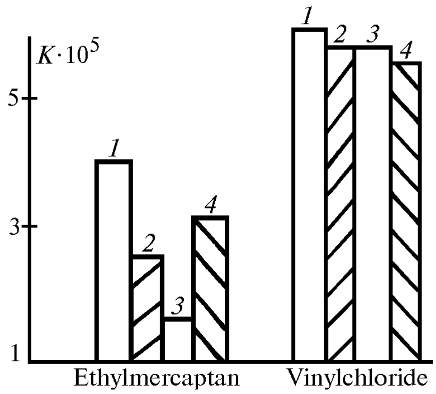

FIG. 1. Results of numerical experiment on reconstruction of ethylmercaptan and vinylchloride concentrations in an 8-component mixture.

Mathematical simulations were made for mixtures with the component number varying from two to eight. Figure 1 depicts the results of numerical experiment on the concentration reconstruction for an 8-component mixture using the regularization procedures. The experiment was carried out by a closed procedure. The values in the right-hand side of the equations from the set (1), $y(\lambda_i)$, were calculated from given values of the gas concentrations and their absorption coefficients. To imitate measurement noise, y values obtained were distorted by random numbers. The noise was simulated by a random process with the uniform distribution, zero mean, and a preset variance. K_a values were assumed equal zero. As shown in Fig. 1, the values *1* are preset concentrations, whereas *2*, *3*, and *4* give reconstructed concentrations for the regularizing parameter selected based on the modified principle of discrepancy, the principle of discrepancy (5) and by choosing the quasioptimal value of the parameter (6), respectively. The calculations were performed for 8-component ammonia-chloroprene-ethylene-trichlorethylene-isopropanol-vinylchloride-ethylmercaptan-1,2 dichlorethane mixture (for 9.441, 9.550, 9.567, 9.601, 10.156, 10.192, 10.204, 10.230, 10.258, 10.346, 10.455, 10.492, 10.529, 10.588, 10.603, 10.716 μm spectral channels). Reconstructed concentrations of vinylchloride and ethylmercaptan are presented in Fig. 1.

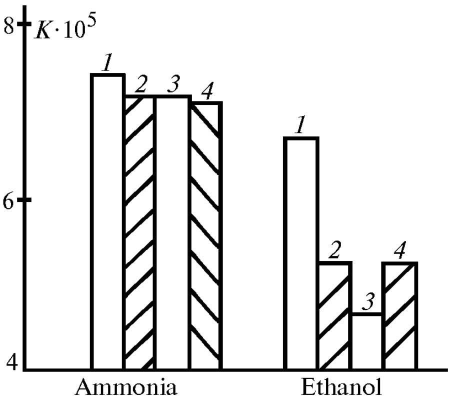

FIG. 2. Results of reconstruction of ammonia and ethanol concentrations for 6-component mixture.

Processing of LPGA signals was made for mixtures with number of components varying from three to six. Figure 2 illustrates the results of reconstruction of ammonia and ethanol concentrations from the experimental data for 6-component ethylene-carbon dioxide-ammonia-methanol-ethanol-isopropanol mixture (for 10.140; 10.200; 9.100; 9.180; 9.120; 9.160; 9.320; 9.340; 9.420; 9.400; 10.120; 10.300 μm spectral channels). Designations in Fig. 2 are identical to those in Fig. 1. Concentration of the components was checked by partial pressure measurements. Measurement procedure and the laser gas analyzer are described in Ref. 11. Relative variances of measurement noise in the spectral channels were estimated in statistical terms from a set of test measurements in the corresponding channels. Concentrations reconstructed using ordinary method of solving of a set of algebraic equations are not presented in Figs. 1 and 2 since these concentrations differ significantly (by one or two orders of magnitude) from the true and reconstructed ones.

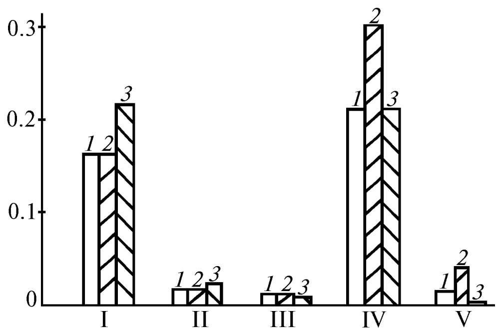

FIG. 3. Relative reconstruction errors of component concentrations for 6-component mixture obtained from experimental data.

Figure 3 depicts relative errors in reconstruction of ethylene (I), ammonia (II), methanol (III), ethanol (IV) and isopropanol (V) concentrations (the absolute differences between the true concentration values and the reconstructed values divided by the true value) after processing of experimental data on 6-component ethylene-carbon dioxide-ammonia-methanol-ethanol-isopropanol mixture (the errors in CO_2 reconstructed concentration are extremely high and, therefore, are not presented). Curves *1*, *2*, *3* present relative errors in concentration reconstruction for the regularizing parameter selected based on the modified principle of discrepancy, the principle discrepancy (5) and by choosing the quasioptimal value of the parameter (6), respectively.

As the figures show, in the majority of cases regularization processing procedures for 6- and 8-component mixtures provide relatively low errors in reconstructed gas concentrations for different methods of selection of the regularization parameter. The modified method of discrepancy in selection of the parameter provides the errors in concentrations of all gases to be lower than or equal to those obtained in the case of the method of selection of the regularization parameter based on the principle of discrepancy (5). If we designate the relative errors resulted from selection of the regularization parameter based on modified principle of discrepancy, the principle of discrepancy (5) and by choosing the quasioptimal value of the parameter as Δ_1, Δ_2, Δ_3, respectively, then $\Delta_2 \le \Delta_1 \le \Delta_3$ or $\Delta_3 \le \Delta_1 \le \Delta_2$ for all gases. In many cases, selection of the parameter based on the modified principle of discrepancy results in smoothing of reconstruction errors obtained in selection of the parameter based on the principle of discrepancy (5) or in selection of quasioptimal value of the parameter (6).

REFERENCES

1. Yu.S. Makushkin, A.A. Mitsel', and G.S. Khmelnitskii, Zh. Prikl. Spektrosk. **35**, No. 5, 785–790 (1981).

2. R.M. Measures, *Laser Remote Sensing* (Willey, New York, 1987).

3. S.V. Ivanov, V.Ya. Panchenko, and T.B. Razumikhina, Atmos. Oceanic Opt. **6**, No. 8, 989–992 (1993).

4. Yu.N. Ponomarev, *ibid*. **8**, Nos. 1–2, 116–124 (1995).

5. M. Zigrist, M.Yu. Kataev, A.A. Mitsel', et. al., *ibid*. **7**, Nos. 11–12, 795–799 (1994).

6. Yu.E. Voskoboinikov, N.G. Preobragenskii, and A.N. Sedelnikov, *Mathematical Processing of Experiment in Molecular Gas Dynamics* (Nauka, Novosibirsk, 1984), 238 pp.

7. Yu.E. Voskoboinikov, M.Yu. Kataev, and, A.A. Mitsel', Atmos. Opt. **4**, No. 2, 151–158 (1991).

8. S.L. Bondarenko, S.N. Dolgii, and V.V. Zuev, Atmos. Oceanic Opt. **5**, No. 6, 386–399 (1992).

9. A.N. Tikhonov and V.Ya. Arsenin, *Solution Techniques for Ill-Posed Problems* (Nauka, Moscow, 1979), 288 pp.

10. L.S. Rothman, R.R. Gamache, et.al. J. Quant. Spectrosc. Radiat. Transfer. **48**, 469–507 (1992).

11. V.I. Kozintsev, Atmos. Oceanic Opt. **2**, No. 8, 689–691 (1996).