

LASER PHOTO-ACOUSTIC GAS ANALYZER FOR MONITORING COMPOSITION OF MULTICOMPONENT GAS MIXTURES

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Received June 30, 1995

We present here some results of reconstruction of concentrations of gaseous constituents in a six-component mixture of ammonia, ethylene, methanol, isopropanol, carbon dioxide, and ethanol. It is shown that the use of regularization procedures for data processing allows significant improvement in the accuracy of reconstruction of gas concentrations in a gas mixture of six and more components. As a radiation source, we used a tunable CO₂ laser that generates 65–70 lines in the 9–11 μm spectral range with the output power of 1–3 W. Data processing used the modified method of regularization parameter selection based on the principle of discrepancy.

Nowadays the environmental protection is one of the most important problems. Laser methods seem to be most promising for prompt monitoring of gas pollution and therefore their application to ecological monitoring of the atmosphere is of great interest. Among such methods is the laser photo-acoustic (PA) spectroscopy allowing the measurements of pollutant concentrations promptly, with high accuracy, and within a wide concentration range.^{1,2}

This paper describes an operating measurement complex for estimating gas concentrations in the multicomponent gas mixtures for ecological and technological control of their composition. Good performance of this complex is demonstrated. Some examples are presented of its experimental testing, that allow estimation of its accuracy in reconstruction of gas concentrations.

The measurement complex comprises a laser photo-acoustic gas analyzer with a nonresonance cell and an IBM personal computer with the software implementing the algorithm for measurement process control and automation. The programs developed provide for measurement results processing and displaying the output information about pollutant concentrations. Figure 1 shows the block diagram of the measurement complex. It comprises a CO₂ laser 1, a PA cell 2, an MG-30 photodetector 3, a KMS-19 microphone 4, a chopper 5, an optical sensor 6, a modulation frequency stabilization unit 7, an interface card 8, a CO₂-laser frequency control 9, a pump unit 10, a V3-60 ac voltmeter 11, an exhaust unit 12, a beam-splitting mirror 13, and a personal computer 14.

It is a peculiar feature of the measurement complex that the CO₂ laser used is an entirely metal construction with the medium excitation with a high

frequency field. The laser can be tuned in 9.1 to 10.8 μm. It is also specific of this complex that it uses regularization algorithms for solving ill-posed mathematical problems.

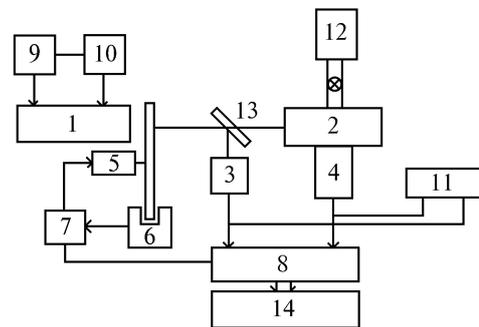


FIG. 1. Block diagram of the measurement complex.

The measurement facility uses a PA cell. The radiation is emitted by the CO₂ laser generating 65–70 lines in the 9–11 μm spectral range at the output power of 1–3 W. The laser radiation, modulated at a frequency of 125 Hz by the chopper, is directed into the PA cell. The acoustic oscillations excited in the cell under the exposure to laser radiation are recorded with a microphone. Optical radiation power in the reference channel is recorded with a photodetector built around the MG-30 chip. The signals enter the interface card of the personal computer, where the synchronous detection and digital processing are done. For the visual control over the operation of the measuring unit of the interface card, the signal amplitude is recorded with an ac voltmeter. The unit 7 serves for modulation frequency stabilization. The

reference voltage generated by the optical sensor also enters the interface card. The exhaust unit provides for preparation, fill-in, and purging of the PA cell with a multicomponent gas mixture to be analyzed. The measurement complex was calibrated with a specially prepared ethylene–nitrogen mixture. The ethylene concentration in the mixture was determined accurate to 6%. By adding pure nitrogen to the calibrating and analyzed mixtures, the total pressure of 1 atm was established in the PA cell for modeling the collisional broadening of the absorption line profiles in the atmosphere. The pump and automatic frequency control (AFC) units provide for CO₂ laser operation. The measurements are conducted in turn at M pairs of wavelengths (M is the number of gases in the mixture, i.e. a total of $2M$ wavelengths). The measurements are done at a pair of wavelengths for each gas in order to take the account of nonselective absorption when reconstructing the concentrations of gaseous constituents in the mixture. Wavelengths in pairs are chosen close to each other. One wavelength is chosen to be coincident with the absorption peak of the gaseous constituent to be estimated at this pair, and another wavelength is chosen out of the absorption peak of all gases in the mixture. No other special requirements were imposed when choosing the wavelengths for analyzing the gas mixture composition.

As the gases to be analyzed, we have selected chemically noninteracting substances, such as ammonia, ethylene, carbon dioxide, ethanol, methanol, isopropanol, acetone, dichlorethane, and other organic gaseous substances. The measurements were done with two-, three-, four-, five-, and six-component mixtures.

Multicomponent gas mixture to be analyzed was prepared in the following way. The exhaust unit involves a settling chamber for preparing gas mixture. It was first pumped out down to pressure about 10^{-3} atm. Then the bottles with solutions of gaseous components under study (ethanol, methanol, isopropanol, etc.) were connected to it in turn following special technique. The pressure changes (partial pressures) in the settling chamber due to the inflow of saturated vapors of gases under study into it were measured using a VIT-2 ionization-thermocouple vacuum gauge accurate to 6% and better. Then pure nitrogen was added into the settling chamber up to the pressure of 1 atm.

The program for measurement results processing is based on the methods of solution of ill-posed mathematical problems and construction of regularized solution to the system of equations for parameters measured.^{3,4} The main problem in obtaining a regularized solution is the choice of the regularization parameter α . One of the widely used methods of choosing α is based on the discrepancy principle. The parameter of regularization is found from the equation^{3,4}:

$$\|W \mathbf{x}_\alpha - \mathbf{y}\| = \delta^2,$$

where $\|\mathbf{z}\|$ is the norm of the vector \mathbf{z} ; W is the matrix of the system of linear algebraic equations to find the gas concentrations from photo-acoustic signals (see, for example, Ref. 1); \mathbf{x}_α is the regularized solution to the system of equations for gas concentrations (the vector of reconstructed gas concentrations); \mathbf{y} is the vector of photo-acoustic signals measured. The parameter δ^2 has the meaning of measurement noise variance.

When processing measurement data in order to obtain the regularized solution (to reconstruct the concentrations of gaseous components), we used the modified method of regularization parameter choice based on the discrepancy principle. This modified version allowed us to decrease a little the errors of reconstruction of the pollutant concentrations at a wide variety of noise in different channels (in contrast to usual discrepancy method,^{3,4} the modified version takes into account the difference in the measurement noise variance in different spectral channels). The absorption coefficients of gaseous components at the wavelengths of measurement spectral channels, the photo-acoustic signals measured, and measurement noise variance (δ_i) in spectral channels served as the initial data for the algorithm of reconstructing the concentrations of gaseous components. The values δ_i were statistically estimated from the results of series of test measurements in the spectral channels. The procedures of photo-acoustic signal processing are realized as the software package for IBM PC.

The processing results show that for two-, three-, and four-component gas mixtures the errors in reconstruction of the gas component concentrations are usually small, and the use of regularization procedures in data processing does not improve the accuracy of the reconstruction. A slight increase in the accuracy is observed for a five-component mixture, and when dealing with mixtures of six and more components the accuracy of reconstruction of the component concentrations increases significantly with the use of regularization procedures.

Figures 2–4 show some examples of results on reconstruction of the concentration (in relative units) of gas mixture components. In processing we used the average (over 10 experiments) values of signal from the gas analyzer. For a comparison the figures show the concentrations obtained with the use of regularization procedures of processing (curves 1); the data obtained by usual method of solution of the system of linear algebraic equations (curves 2); and the true value of concentrations of gas components determined from partial pressure when filling the cell (curves 3). The reconstructed concentrations of the gas components (K) are laid out as an ordinate.

The measurements were conducted for a six-component gas mixture ethylene–carbon dioxide–ammonia–methanol–ethanol–isopropanol (at the sensing wavelengths 10.140, 10.200, 9.100, 9.180, 9.120, 9.160, 9.320, 9.340, 9.420, 9.400, 10.120, and 10.300 μm).

It is seen from the figures that the use of regularization procedures for processing provides for much lower level of the reconstruction errors. If used for processing the results of single measurements (rather than averaged over 10 experiments), the advantage of the regularization procedures over usual method of processing becomes more obvious.

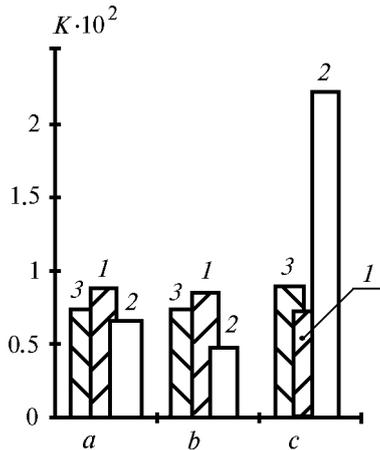


FIG. 2. The results of reconstructing the concentration of ammonia (a), methanol (b), and ethanol (c).

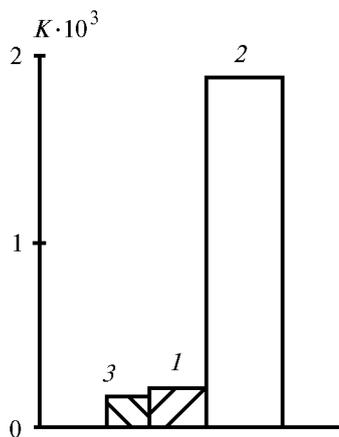


FIG. 3. The results of reconstructing the concentration of ethylene.

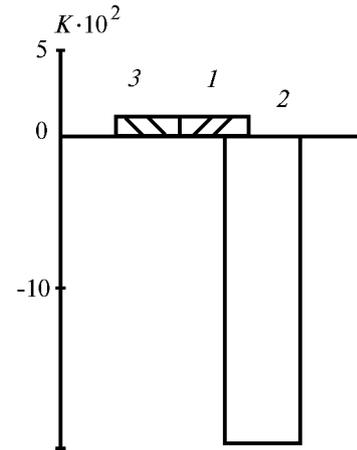


FIG. 4. The results of reconstructing the concentration of isopropanol.

Thus, in this paper we have described the measurement complex for monitoring the composition of multicomponent gas mixtures using a laser photoacoustic gas analyzer tunable within 9.1–10.8 μm range and implementing the signal processing algorithms based on the methods of constructing the regularized solutions to ill-posed mathematical problems. The use of such a measurement complex allows significant improvement in the accuracy of reconstruction of gas concentration for gas mixtures of six and more components as well as in reliability of the control of emissions from industrial enterprises.

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