

LASER GAS ANALYSIS OF MULTICOMPONENT MIXTURES WITH OVERLAPPING SPECTRA: THEORY AND COMPUTER PROGRAM FOR DATA PROCESSING

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A technique is developed for data processing in laser gas analysis of multicomponent mixtures with overlapping spectra. The case of nonmonochromatic sounding radiation is considered. Numerical experiments on solving the direct and inverse problems of laser gas analysis of three-component mixtures are performed.

INTRODUCTION

Laser methods are most promising for operative remote gas analysis of multicomponent mixtures and are of great interest for atmospheric ecology, medicine and other fields.¹ At the same time their practical implementation is difficult due to the following circumstances: (1) insufficiently wide spectral range of sounding radiation,^{2,3} (2) inexact monochromaticity of radiation, and (3) possible overlapping of the absorption spectra of different components of the mixture.³ Infrared laser spectrometers based on PLG,⁴⁻⁶ smoothly tunable in a wide frequency range and processing much higher radiation intensity than semiconductor lasers are much promising candidates for optical gas analysis. At the same time the radiation produced by these devices is not exactly monochromatic. The spectrometer with a radiation line width of 0.2–0.3 cm⁻¹, the tuning range from 2.5 to 4 μm, the pulse duration ~ 15 ns, and the radiation peak power of 5 kW is described in Ref. 6. Practical use of such a spectrometer for simultaneously determining the concentration of several pollutants with overlapping absorption spectra is now hampered by the absence of corresponding computer programs for data processing. This paper concerns the development of theoretical basis for creating such computer programs.

BASIC EQUATIONS

Let us consider the mixture of N gases with absorption bands within the tuning range of a laser spectrometer. At the first stage, it is assumed that the attenuation of the sounding radiation is only due to absorption by molecular components of the mixture. Taking into account nonmonochromaticity of radiation we shall use the integral form of Bouguer law for the medium transmission at the i th laser line and along the path within the length z

$$T_i = \int G_{\text{las}}(v - v_i) \exp \left[-z \sum_{j=1}^N \sigma_{ij}(v) n_j \right] dv, \quad (1)$$

where v_i and $G_{\text{las}}(v - v_i)$ are the center and the normalized to unity spectral profile of the i th line of sounding radiation, n_j is the partial concentration of the j th absorbing gas of the mixture, and $\sigma_{ij}(v)$ describes the spectral dependence of the absorption cross-section of the j th component of the mixture within the spectral profile Ω_i of the i th line. The integration in Eq. (1) is made over the radiation spectrum Ω_i .

Relation (1) includes N unknown concentrations n_j , which can be determined from measurements of the transmissions T_i at N different frequencies of sounding radiation ($i = 1, 2, \dots, N$) and from subsequent solution of a system of N nonlinear equations (1). Note that, if the laser radiation is considered to be monochromatic as it is usually done in the majority of papers devoted to laser gas analysis (see, for example, Refs. 3 and 7), then the system of equations (1) can be drastically simplified and reduced to the analytically resolvable system of N linear nonhomogeneous equations

$$z \sum_{j=1}^N \sigma_{ij}(v_i) n_j = -\ln T_i. \quad (2)$$

It is natural to use the result of solution of Eq. (2) as the zero approximation for numerical solution of more complicated equations (1).

It should be noted that system (1) is the system of coupled equations because it takes into account the possibility of overlapping of the absorption spectra, i.e., all gases of the mixture considered contribute into the attenuation of the i th laser line. In a particular case of weak overlapping the system of equations (1) is decomposed into N independent nonlinear equations analyzed earlier in Ref. 8.

Use of equations (1) for determining the composition of multicomponent mixtures is hampered by the fact that in the real atmosphere the values of the transmission T_i depend not only on selective absorption of molecules of the mixture but also on different types of continuum absorption, scattering, losses due to beam folding mirrors, etc. Because all these types of radiation attenuation have relatively weak spectral dependence, it is convenient to use the differential absorption method for their removal. In this case other system of N nonlinear equations should be solved instead of Eqs. (1)

$$\frac{T_i}{T_{i'}} = \frac{\int G_{\text{las}}(v - v_i) \exp \left[-z \sum_{j=1}^N \sigma_{ij}(v) n_j \right] dv}{\int G_{\text{las}}(v - v_{i'}) \exp \left[-z \sum_{j=1}^N \sigma_{i'j}(v) n_j \right] dv}, \quad (3)$$

where i and i' are the indices of resonance (on) and off-resonance (off) laser lines. Note that in the case under study it is necessary to measure the transmission at $2N$ laser frequencies. To achieve the maximum concentration sensitivity of the method the pairs of frequencies v_i and $v_{i'}$,

should be tuned to the center and to the wing of the most intense absorption lines of the gases, present in the mixture. At the same time it is worthwhile to choose weaker absorption lines if the concentrations of gases under study are high.

SPECTRAL DEPENDENCE OF THE ABSORPTION CROSS-SECTIONS

Spectral behavior of the absorption cross-section $\sigma_{ij}(\nu)$ within the intervals Ω_i , Ω_j , can be calculated using databases of the spectral line parameters (see, for example, Refs. 9–11), or can be measured experimentally. In the first case

$$\sigma_{ij}(\nu) = \sum_{\kappa} S_{j\kappa} f(\nu - \nu_{j\kappa}),$$

where $\nu_{j\kappa}$, $S_{j\kappa}$, and $f(\nu - \nu_{j\kappa})$ are the center, the integral strength and the normalized to unity line profile of the κ th absorption line of the j th gas. The information on $\nu_{j\kappa}$, $S_{j\kappa}$ and the spectral profiles of the absorption lines is usually described by the Voigt line shape.

The matter is different when the information on parameters of the absorption lines of a gas in the mixture is not available. In this case it is necessary to determine the functions $\sigma_{ij}(\nu)$ from specially calibrated measurements for each of the j th gas separately. The simplest way to do this is to use Taylor series expansion of $\sigma_{ij}(\nu)$ in the vicinity of the frequency ν_j and to make as many measurements of the transmission T_i as the number of terms in the Taylor series expansion. When the concentration n_j of the j th gas in the cell is known the unknown coefficients of the expansion can be found by solving the system of equations (1). The series expansion allows one to find an analytical approximation of the cross-section $\sigma_{ij}(\nu)$ within the interval Ω_j . For the majority of complex molecules such a procedure is justified by the absence of drastic changes in the absorption spectrum.¹¹ Note that absence of detailed information on the spectral line parameters for the majority of complex polyatomic compounds is rather the rule than exception. It is connected with very high density of their vibrational rotational spectra. Thus, for example, the average separation between the lines in the ν_3 band of CF_2Cl_2 in the range 921–923 cm^{-1} is about $4 \cdot 10^{-5} \text{ cm}^{-1}$ (see Ref. 11). The processing of such spectra with high resolution is now impossible.

COMPUTER PROGRAM FOR DATA PROCESSING

The program developed for determining the unknown concentration of gases of the mixture considered consists of three subroutines SIG, MIX, and ZSYSTEM. The measured ratios of transmission are used as input parameters along with pressure, temperature and qualitative composition of the mixture, path length and spectral line profiles.

The subroutine SIG calculates and stores the spectral dependences of the absorption cross-sections $\sigma_{ij}(\nu)$ in the intervals Ω_j , which are as large as twenty half-widths of the laser radiation lines (i.e., about 2 cm^{-1}) into an output file. The calculations use either the Rothman's database,^{9–10} or the coefficients of Taylor series expansion (for the spectra with a unresolved fine structure). This subroutine includes the calculation of the Voigt function as well.

The spectral information prepared by the subroutine SIG is used by the main routine MIX to determine concentrations n_j from measured values T_i/T_j by solving system (3). This routine includes the calculation of the left-hand sides of Eqs. (3) reduced to the form $F(n_1, n_2, \dots, n_N) = 0$, solution of the system of linear equations (3) by the Gauss method, and the integration by the Simpson method.

The subroutine ZSYSTEM from the program library IMSL performs the solution of the system of nonlinear equations by the Newton vector method.

RESULTS OF TEST CALCULATIONS

Verification of the program was made in the case of the mixture of three gases: CH_4 , HCl , and H_2CO . The numerical experiment on determining concentrations of the above gases was performed. First, the transmissions T_i and T_j , were calculated using known concentrations and then the inverse problem on determining the initial concentrations from the system of equations (3) was solved.

The conditions under which the test calculations were made are shown in the Table I. The spectral range of sounding radiation was chosen so that it provided for minimum contribution from water vapor into the radiation absorption. The concentrations of HCl and H_2CO used in calculations are typical for the atmospheric pollutions¹ (1–5 ppm for HCl and 0.05 ppm for H_2CO). The methane concentration of 1.5–5 ppm is nearly its background content in the atmosphere^{1,12}.

TABLE I. Conditions used in test calculations.

Set	Sounding channel	$\nu_{\text{on}}, \text{ cm}^{-1}$ $\nu_{\text{off}}, \text{ cm}^{-1}$	Gas	n , ppm	z , km	$T_{\text{on}}/T_{\text{off}}$
1	1	2943, 758 2939, 5000 2963, 2849	H_2CO	5	0.1	0.88
	2	2970, 5000 2948, 4741	HCl	5	0.1	0.45
	3	2950, 7000	CH_4	5	0.1	0.75
2	1	2943, 1758 2939, 5000 2963, 2849	H_2CO	5	0.5	0.55
	2	2970, 5000 2948, 4741	HCl	5	0.5	0.16
	3	2950, 7000	CH_4	5	0.5	0.34
3	1	2943, 1758 2939, 5000 2963, 1000	H_2CO	0.05	30	0.56
	2	2970, 5000 2948, 8000	HCl	0.05	30	0.47
	3	2950, 7000	CH_4	1.50	30	0.13

Numerical experiment showed that the gas concentrations could be determined exactly if the input parameters were also exact. The main source of errors in determining concentrations in actual experiments is uncertainty in the transmission measurement data. The dependences of the error ε_n in determining the gas concentrations on the error ε_T in measuring the ratio of transmissions $T_{\text{on}}/T_{\text{off}}$ in sounding channels are shown in Figs. 1a and b. Since the errors in measuring the transmission may be different in different sounding

channels, we have considered two different ways of introducing perturbations into the channels. According to the first one the experimental error causes an increase of the ratio T_{on}/T_{off} in one channel and corresponding decrease of this value in two other channels, and in the second one the experimental error leads to the proportional decrease of the relative transmittance in all three sounding channels.

It can be seen from Fig. 1 that in the cases considered the error in determining the H_2CO concentration is always maximum. The error ϵ_n strongly depends on the value of contrast (the ratio T_{off}/T_{on}) for the absorption line of a given gas. The experimental error decreases when the contrast increases.

It follows from the comparison of Figs. 1a and b that the sensitivity of the error ϵ_n to the way of introducing perturbations into the measuring channels also decreases with increasing contrast. Similar results were obtained for an extended path (see the case 3 in the Table). Thus, for example the error in transmittance $\epsilon_T \approx 10\%$ resulted in the errors of determining CH_4 of 5–8%, HCl – 13–20%, and H_2CO – 34–65%. The analysis shows that the sensitivity of the error in determining concentrations to the way of introducing perturbations into the measuring channels depends on the degree of overlapping of the absorption lines of the gases under study.

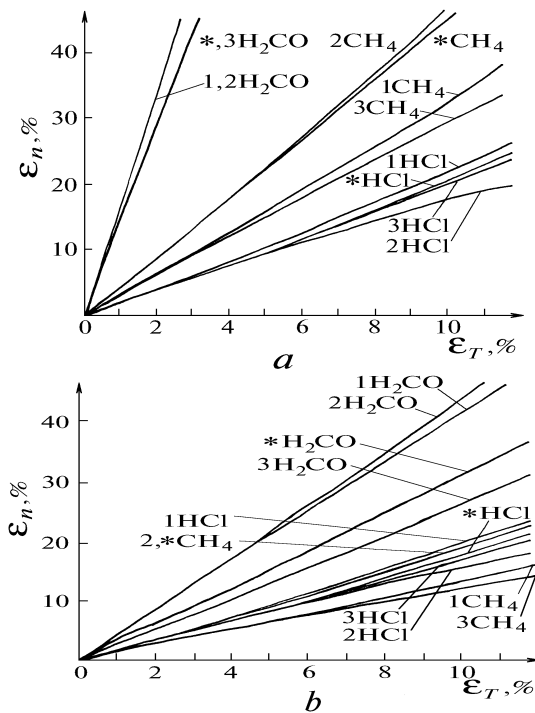


FIG. 1. Dependence of the error in determining the gas concentrations ϵ_n on the error ϵ_T in measuring the ratio of transmittances T_{on}/T_{off} in sounding channels. Numbers near curves denote the numbers of channels in which the errors in measurements increase the ratio T_{on}/T_{off} at correspondingly decreasing T_{on}/T_{off} in the other two channels. The asterisks at curves correspond to the case of proportional decreasing T_{on}/T_{off} in all three sounding channels. a) calculation under conditions 1 and b) calculation under conditions 2 (see the Table I).

The errors in determining concentrations can also appear at the data processing stage because of uncertainties in the parameters of the laser emission lines. The dependences of the error ϵ_n on the shift δv_{las} of sounding radiation lines and on the errors ϵ_c in half-widths of the laser lines are depicted in Figs. 2a and b, respectively. It is seen from these figures that at the frequency shift $\delta v_{las} \lesssim 0.05 \text{ cm}^{-1} \approx 0.5\gamma_{las}$ the error in determining concentrations of all gases does not exceed 25%, and at the error in half-width $\epsilon_c \lesssim 10\%$ $\epsilon_n \lesssim 15\%$ for all gases. It follows from the simple considerations that the sensitivity ϵ_n to δv_{las} and ϵ_c depends on the structure of absorption spectra in the vicinity of frequencies ν_{on} and ν_{off} .

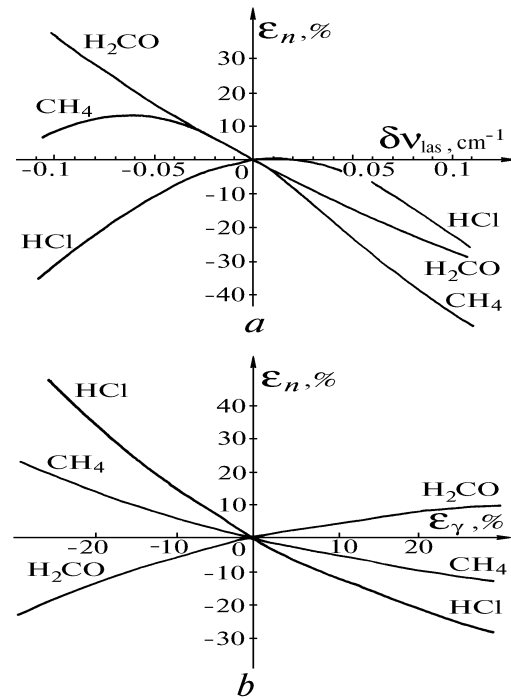


FIG. 2. Dependence of the error in determining the gas concentrations ϵ_n (a) on the uncertainty $\delta\nu_{las}$ in frequencies of the sounding radiation lines ($\nu'_{on,off} = \nu_{on,off} + \delta\nu_{las}$) and (b) on the error ϵ_γ in the half-widths of the sounding radiation lines.

In more complicated cases (large number of gases in the mixture, strong overlapping of the spectra, small contrast T_{off}/T_{on}) the problem in determining the concentrations becomes extremely sensitive (unstable) to the errors in transmission and to the uncertainties in the parameters of laser radiation. To obtain a stable solution of this problem the method of statistical regularization can be used, see, for example, Refs. 3 and 13. Besides, in a more complicated case of gas analysis the error in determining concentrations can be reduced if smooth tuning of the frequency of the laser spectrometer within a wide range is available. Such a tuning allows one:

- 1) to support the transmission of radiation at the level necessary to minimize the instrumental errors by properly choosing ν_{on} and ν_{off}
- 2) to choose ν_{on} and ν_{off} in such a manner that the absorption line overlapping of the gases under study is minimum,

3) to use the method of differentiating the transmission spectra for essentially increasing the concentrational sensitivity of the gas analysis.

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