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Determination of the concentration of CO_2 and H_2O vapor under conditions of overlapping spectral lines

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Abstract. The efficiency of determining the concentration of CO_2 and H_2O vapors in the atmosphere has been investigated taking into account the overlap of their spectral lines. It is proposed to use regression relationships established between the determined and measured parameters of the investigated medium. These ratios can be set both for fixed values of temperature and pressure, and for a set range of their values. When calculating the absorption value, all overlaps of spectral lines are taken into account, taking into account their broadening at different temperatures and pressures. This allows the method to be used in multicomponent media with strongly overlapping spectral lines. The established regression relations are resistant to errors in the measurement information, which also improves the accuracy of determining the concentrations of the component composition of the gas medium. In addition, they are determined promptly (in real time), since the calculation of concentrations using established relationships (analytical expressions) between the determined and measured values does not present computational difficulties.

1. Introduction

Any chemical compound has its own emission or absorption spectrum, and the form of the obtained spectra can be used to determine its composition, that is, to carry out a qualitative analysis [1]. The most commonly used optical method is the differential method. Based on absorption measurements at two wavelengths λ_0 and и λ_1[2]. By the values of the absorption values, the concentration of the determined gas is judged. The destabilizing factors that form the measurement errors of this method include: instability of the instrumental constants of the receiving and emitting devices, variations in the content of accompanying components in a controlled aerodispersed medium, and changes in atmospheric pressure and temperature.

For multicomponent media, when their spectral lines overlap, multispectral measurements are used (combinations of wavelengths are established [3–5]), which require solving the inverse problem. In this case, the problem of finding the concentration of gas components from the measurement results belongs to the class of incorrect mathematical ones. The solution of such problems can be unstable in relation to small variations (errors) of the measured data, leading to large errors in determining the component composition of the mixture [3, 6].

Typically, all algorithms for solving inverse problems are based on comparing the measurement results with a function describing the relationship of the recorded signals with the parameters of the investigated medium, or they use calibration models obtained in advance using empirical (experimental) modeling [4]. A set of parameters is found such that their difference is minimal. As noted in [5], the solution to the inverse problem essentially depends on: 1) the type of the chosen physical model of the medium and the approximations; 2) on the volume and quality of a priori information; 3) dimensions of the vector of unknown parameters and measured values; 4) on the quality of determining the characteristics of the measurement error. The specified features of the solution, on the one hand, make it possible to obtain the appropriate quality of the solution

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(assessment). However, these estimates are very time consuming for large dimensions of the measurement vector; significantly depend on the magnitude of the error, they can receive physically incorrect results when deciding (zeroing, negative values, etc.); require a correct and careful choice of the physical model and approximations [5].

The task of monitoring multicomponent gaseous media is even more complicated when their spectral lines overlap strongly. In this case, the use of the selected spectral measurement channels corresponding to the absorption lines of the components under study requires taking into account the contribution of their overlap [7].

A new approach to solving the inverse problem of optical sounding based on the establishment of regression relationships between the determined parameters and the measured optical characteristics was proposed in [8]. In this paper, we consider the possibility of using this approach to determine the concentrations of water vapor and carbon dioxide in the atmosphere from spectral measurements in the range of 2660–2840 nm, in which their absorption lines overlap most strongly.

2. Method

The regression method for solving inverse problems assumes that the desired parameters of the medium (in particular, the concentration of gas components) can be found using some statistical function of the measured optical characteristics. In this work, linear multiple regressions were used as a functional connection between the percentage concentration M of water vapor (meaning the main isotope of water H_2O) and CO_2 (meaning the main isotope of carbon dioxide CO_2) and the spectral absorption $I(\lambda i)$.

From the point of view of the promptness of determining the concentrations of the component composition of the gas mixture, it is of interest to calculate them on the basis of an analytical expression connecting them with the main components C_m of the spectral absorption vector $\vec{I}(\lambda_i)$ for the wavelengths used n. Such an expression can be obtained on the basis of measurements or numerical calculation of $I(\lambda i)$ for a variety of situations or phantoms modeling it with known values of the concentrations $M_{k,P,T°K}$ of the component composition of the gas mixture at various values of its temperature T°K and pressure P (i.e. broadening of spectral lines with their change) and subsequent regression analysis establishing a relationship between $M_{k,P,T°K}$ and C_m. In particular, regression relations can be used as such an expression [8–9]

$$M_{k,P,T^oK} = a + \sum_{m=1}^{N} b_m C_m, \tag{1}$$

where N is the number of principal components.

The values $I(\lambda i)$ can be viewed as components of the random vector $\vec{I}(\lambda_i)$. We expand the vector $\vec{I}(\lambda_i)$ in terms of the system of orthonormal basis vectors (principal components) [9]

$$\vec{I}(\lambda_i) = \overline{\vec{I}(\lambda_i)} + VC_m,$$

where V is a matrix with columns of principal components C_m, the numerical values of which are determined as the projections of the vector$\vec{I}(\lambda_i)$ onto the space of principal components and are found as follows

$$C_m = V^t\left(\vec{I}(\lambda_i) - \overline{\vec{I}(\lambda_i)}\right), \tag{2}$$

where the subscript t denotes the transposition operation. Due to the fast convergence of the considered expansion, the first basis vectors account for most of the variability of the vector $\vec{I}(\lambda_i)$, and the corresponding principal components contain practically as much information as was in the initial data. Consequently, to reconstruct the concentrations of the component composition of the gas mixture $M_{k,P,T°K}$, one can use not the measurement vector itself, but its main components.

The numerical value of a, b_m is determined by calculating the principal components C_m by formula (2) for all realizations I (λi), each of which corresponds to a specific value of $M_{k,P,T^\circ K}$, and using the least squares method to approximate the statistical relationship between C_m and $M_{k,P,T^\circ K}$.

After obtaining the vectors $\vec{I}(\lambda_i)$ and the average vector $\vec{I}(\lambda_i)$, V, as well as the aforementioned analytical expression (1), they can be used to determine the concentrations of the component composition of the gas mixture from the results of spectral absorption measurements. The numerical value of a, b_m can be set both for each pair of values of pressure P and temperature T°K, as well as for the specified range of their values.

Thus, the determination of the concentration of the component composition of gas mixtures includes the determination of the main components for the values of spectral absorption. Determination of the concentration based on the regression ratio corresponds to a specific temperature and pressure in the mixture at the time of measurements or to a specified range of their values. Interpretation of the measurement information does not require the fulfillment of any conditions or the use of additional information about the state of the investigated medium, the use of calibration comparative models established in advance empirically (experimentally), the use of methods for solving incorrect inverse problems. Resistance to errors in determining the absorption values appears (the establishment of links between the concentration and the measured parameters is carried out taking into account the errors of the measuring equipment).

3. Evaluation of the effectiveness of the method for the specified values of pressure P and temperature

Let us consider in more detail the process of obtaining the main components C_m and the regression coefficients a, b_m using the example of determining the concentration of gas components – the concentration of water vapor H_2O and carbon dioxide CO_2 in the atmosphere. This is an urgent task at the present time in connection with the greenhouse effect, which is associated with the ongoing changes in the climate. CO_2 and water vapor largely determine this effect. The humidity of the atmosphere is also one of the most important meteorological parameters of the atmosphere.

The possibilities of the proposed method will be estimated for the determination of water vapor and carbon dioxide in the atmosphere by spectral measurements of absorption in the range of 2640–2840 nm, in which there is a strong overlap of their absorption lines.

To obtain the principal components and regression coefficients, the absorption process was modeled based on data from the HITRAN database, which serves as a tool for calculating the absorption of light in gaseous media, including the atmosphere [10]. The absorption values $I(\lambda i)$ were calculated in the range of 2640–2840 nm with a step of 20 nm for random values of the concentrations of H_2O and CO_2 vapors in the range from 0.1% to 5% for H_2O and from 0.2% to 3% for CO_2. The measuring base was set with a length of 10 m.

When calculating the simulated sample $I(\lambda i)$ for each temperature and pressure, the broadening of spectral lines from their magnitude was taken into account. Using the obtained values of $I(\lambda i)$, the main components of C_m were identified for each temperature and pressure equal to 1 atm. The size of each of the samples was 2000 states. The results below are obtained for two principal components C_m, which cover 99.9% of the data variability.

The numerical values of the c_{mi} of the principal components are a linear combination of spectral absorption in the range of 2640–2840 nm with a step of 20 nm (for n = 10 wavelengths)

$$C_m = \sum_{i=1}^{10} c_{mi} I(\lambda_i).$$

The cmi factors at the spectral absorption values for the main components C_m are given in table 1.

Then, using the least squares method, a statistical relationship was established between the principal components C_m, the coefficients a, b_m, and the concentrations of the components in the mixture $M_{k,P,T^\circ K}$. Coefficients a, b_m of regression relation (1) for temperature values in the range 253–293 T°K, corresponding to H_2O and CO_2, are shown in figure 1 and 2 (the temperature values T°K are located along the x-axis).

Table 1. Factors at the absorption coefficients for the principal components C_m.

Wavelengths, nm	The values C_{1i}	The values C_{2i}
2660	0.3218	-0.2689
2680	0.3263	0.2245
2700	0.2504	0.6195
2720	0.3285	0.1991
2740	0.3155	-0.3217
2760	0.3336	-0.1175
2780	0.3122	0.3449
2800	0.3348	0.0888
2820	0.3152	-0.3232
2840	0.3151	-0.3240

The estimation of the error in reconstructing the concentrations of H_2O and CO_2 vapors was carried out on a new sample $I(\lambda i)$ with the imposition of an error of 5% on each value of it (sample size – 500). The specified values of the concentrations of H_2O vapors and were compared with the calculated concentrations according to (1). The values of errors for the concentrations of H_2O and CO_2 vapors (for the beginning, middle and end of the temperature range) at are given in table 2. As can be seen from the table, the reduction errors were for H_2O and CO_2 vapors respectively, less than 2% and less than 4%, which indicates the stability of the regression relationships to errors in measuring the absorption values of ~ 5%.

The error in recovering the CO_2 concentration was estimated using the above wavelength range and using the differential absorption method as the most accurate and stable of the recorded signals known to measurement errors (excluding these errors in the absence of overlapping spectral lines of gas components). However, even when using the weakest overlap of spectral lines in a given wavelength range, when determining the CO_2 concentration by this method in a real atmosphere, the errors are more than 80%.

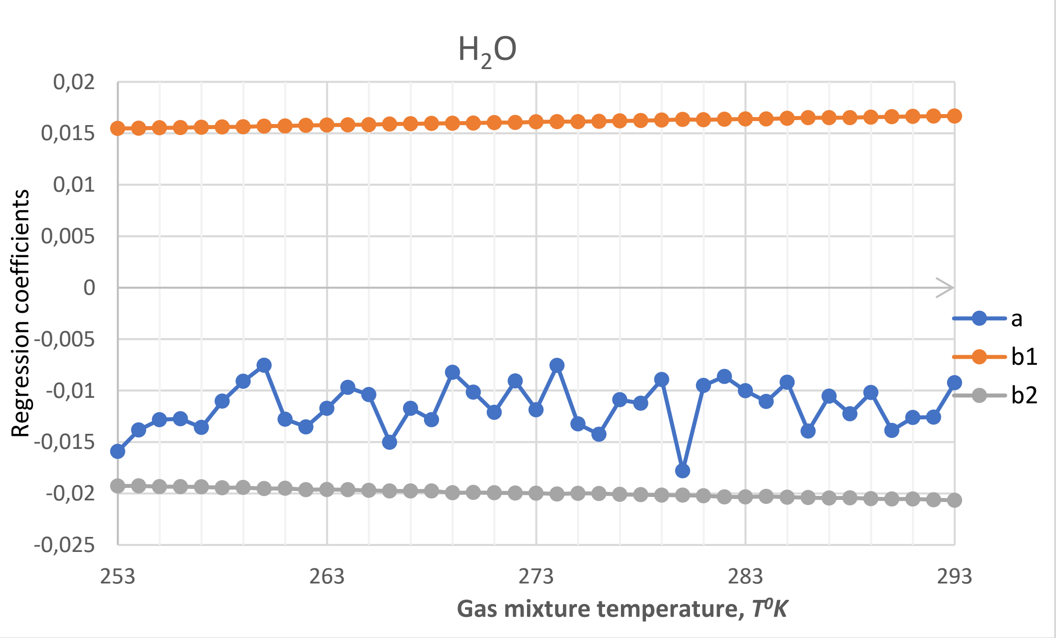

Figure 1. Regression coefficients (5) for temperature values in the range 253–293 T°K (a – middle curve, b1 – upper, b2 – lower).

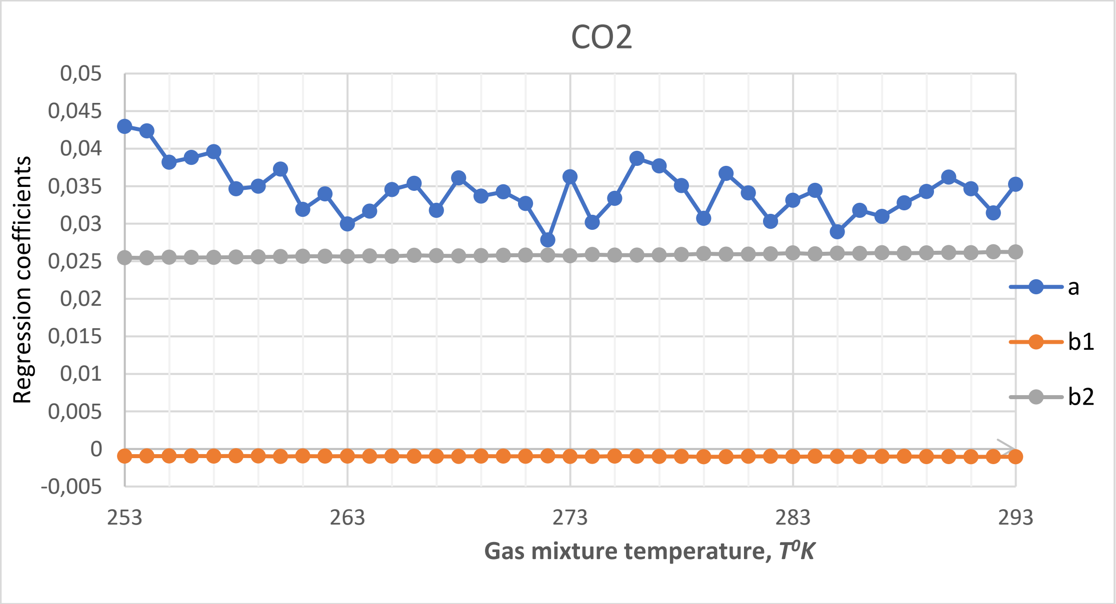

Figure 2. Coefficients of regression relation (5) for temperature values in the range 253–293 T°K (a – the upper curve, b1 – the lower one, b2 – the average).

Table 2. Linear regression coefficients (1) for H_2O and CO_2.

/	H_2O	CO_2
a	-0.0065	0.0299
b_1	0.0168	-0.0009
b_2	-0.0209	0.0265

4. Evaluation of the effectiveness of the method for a given range of values of pressure and temperature

Above, the numerical values of *a*, *bm*, *Cm* were established for each pair of values of pressure *P* (*P* = 1 atm) and temperature T°K and related the concentrations of the components of the gas mixture with the main components of the measurement vector *I*(*λi*). They were installed for a situation when measurements are carried out at known values of temperature and pressure. It is of practical interest to carry out measurements under conditions that do not require knowledge of the pressure *P* and temperature T°K of the gas mixture under study. The numerical value of *a*, *bm*, *Cm* for (1) and in this case are established on the basis of measurements or numerical calculation of *I*(*λi*) for a set of situations or phantoms modeling it with known values of the concentrations M_k of the component composition of the gas mixture at various values of its temperature and pressure, but already in the specified range of their values (for example, for the season, for possible values in technological processes, etc.).

However, if the vector of realizations $\vec{I}(\lambda_i)$ is used for the situation considered above, corresponding to different values of $M_{k,}$ for specific (measured) values of pressure *P* and temperature T°K then in the case under consideration the vector of realizations $\vec{I}$ includes all values of *I*(*λi*), corresponding to different values of $M_{k,}$ for any values of *P* and T°K from the specified range of their spread (the range of changes for M_k, *P* and T°K is specified).

After obtaining the vectors $\vec{I}(\lambda_i)$ and the average vector $\vec{I}(\lambda_i)$, *V*, as well as the above-mentioned analytical expression, they can be used to determine the concentrations of the component composition of the gas mixture from the measured values of *I*(*λi*). This does not require knowledge of the temperature and pressure of the gas mixture.

The capabilities of the proposed method in situations that do not require knowledge of the pressure *P* and temperature T°K of the gas mixture under study were evaluated to determine water vapor and carbon dioxide in the atmosphere by spectral measurements of absorption in the range 2640–2840 nm, in which there is a strong overlap of their absorption lines the same conditions as for the atmospheric situation, when pressures *P* and temperatures T°K are fixed). Linear regression coefficients for temperature values in the range 253–293 T°K, pressure 1 atm. are shown in table 3.

Table 3. Linear regression coefficients (for the specified range of pressure and temperature values).

/	H_2O	CO_2
a	–0.004	0,0368
b_1	0,0161	–0.0010
b_2	–0.0200	0,0258

The values of the errors in determining the concentrations of CO_2 and H_2O vapors in the atmosphere during measurements when the values of pressure P and temperature T°K are not set are 6.1% and 3.6%, respectively.

5. Conclusion

Thus, to determine the quantitative values of the concentration of each component of the gas mixture by the proposed method, it is not required to compare the measurement results with the function describing the relationship (calculation) of the recorded signals with the parameters of the investigated medium, the use of calibration comparative models that are established in advance empirically (experimentally), methods for solving incorrect inverse tasks. In the proposed method, it is required in advance, only once, by numerical modeling of the medium under study (calculating the value of spectral absorption), to establish the coefficients of the regression relationship between the concentration and the main components of the value of spectral absorption for each component of the medium, and use it for this medium under different conditions (temperature, pressure - and they can be set both for fixed values of temperature and pressure, as well as for a given range of values of their values) When calculating the absorption value, all overlaps of spectral lines are taken into account, taking into account their broadening at different temperatures and pressures, which makes it possible to use the method in multicomponent media with strongly overlapping spectral lines. Moreover, the established regression relations are stable to errors in the measurement information, since when they are obtained, these errors are superimposed on the calculated absorption values. All this leads to an increase in the accuracy of the proposed method for determining the concentrations of the component composition of the gaseous medium. In addition, it allows them to be determined promptly (in real time), since the calculation of concentrations using the established relationships (analytical expressions) between the determined and measured values does not present computational difficulties, does not require sampling, since it can be used both in the baseline and in remote implementations.

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