CONDENSED-MATTER SPECTROSCOPY

Substance Recognition in the Open Atmosphere from a Single Fourier Transform Spectroradiometer Interferogram

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Abstract—An in-situ technique for identification of substances in the open atmosphere from the analysis of a single Fourier-transform spectroradiometer interferogram is described. A database of spectra of major atmospheric constituents and typical atmospheric paths is compiled to be used for the calculation of an atmospheric path with the following separation of a pollutant spectrum from the experimentally recorded spectrum. The identification of a substance by its spectrum is performed through sorting out substances from the database by the correlation coefficients and a quantitative analysis is performed by minimizing the discrepancy functional between the experimental and database spectra. The technique described is tested in situ.

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INTRODUCTION

The atmospheric pollution is one of the most pressing problems of modern times, and, consequently, the ecological monitoring of the state of the atmosphere and the permanent monitoring of harmful industrial emissions are urgent. Therefore, it is necessary to develop techniques and instrumentation for the remote sensing of the atmospheric composition in real time with high mobility. Among other optical methods of atmospheric monitoring, Fourier transform spectroradiometric systems are promising [1].

Substances in the open atmosphere can be identified by a direct line-by-line calculation of the spectrum of an atmospheric path including signatures of all substances and surface on the vision line of an instrument [2] using spectral databases, such as HITRAN [3] and GEISHA [4]. However, this procedure requires rather high qualifications from the operator and is time consuming, which makes real-time operation under field conditions impossible. An alternative fast method is the regression analysis of the normalized spectrum of a sought substance in the atmosphere [5, 6]. To calculate the normalized spectrum, the total spectrum of an observation path along with the spectrum of the background surface is recorded in the case of no pollutants in the atmosphere (the relative identification technique). However, in some cases, when the continuous operation under fast varying ambient conditions is necessary, the technique should result in the identification

of substances in the open atmosphere from a single recorded spectrum (the absolute identification technique). The necessity of the analysis from a single spectrum under certain conditions is mentioned in [5]. The technique of analysis of a single spectrum based on the recalculation of a recorded spectrum into the brightness temperature is described in [7]. This method allows the identification of substances. This paper proposes an alternative method of analysis of a single spectrum based on its recalculation into the normalized spectrum, which opens the possibility of the qualitative and quantitative analysis of substances in the open atmosphere in real time.

At the first stage of the analysis, the total normalized spectrum of the observation path is separated. For this purpose, two Planck functions multiplied by the transmission function of the Fourier transform spectroradiometer (FTSR) are inscribed in the spectrum and the normalized spectrum is separated. At the second stage, the atmospheric spectrum is calculated by minimizing the discrepancy functional with a certain penalty function. Finally, at the last stage, database substances are sorted out according to their correlation coefficients. The substance with the highest correlation exceeding some a priori threshold is considered to have been detected in this experiment.

In contrast to classical spectral devices, FTSR does not give the spectral distribution of brightness of an observed object, but rather forms an autocorrelogram.

To obtain the spectrum of an observation path, it is necessary to perform the Fourier transform with the preliminary phase-correction procedure and elimination of the background radiation component from the obtained spectrum [1, 8]. This paper describes an algorithm for the final processing of the spectrum of an observation path.

CALCULATION OF THE NORMALIZED SPECTRUM OF AN OBSERVATION PATH

In processing of spectra of radiation of objects in the atmosphere, the most general form of the radiative transfer equation can be used. However, the solution of this equation is computationally expensive and requires the use of databases on the emission properties of background surfaces and spectral absorption coefficients of observation paths, as well as the knowledge of the weather situation. The problem formulated can be simplified if we assume that the temperatures of gaseous atmospheric constituents on a path are constant. This assumption is justified for near-surface observation paths, for which temperature drops along a path are within several degrees. Then we can write the radiative transfer equation of the so-called "three-layer model" as follows [1]:

$$B = \Phi_0 \tau_{atm} \tau_{sub} + P_{atm}(1 - \tau_{atm}) + P_{sub}(1 - \tau_{sub})\tau_{atm}, \quad (1)$$

where $\Phi_0 = \Phi_0(T, \nu)$ is the radiation of the background surface; $\tau_{atm} = \tau(\nu)$ and $\tau_{sub} = \tau(\nu)$ are the spectral coefficients of the atmospheric path and the substance cloud, respectively; $P_{atm} = P_{atm}(T_{atm}, \nu)$ and $P_{sub} = P_{sub}(T_{sub}, \nu)$ are the Planck functions at the temperature of the atmospheric path and a substance, respectively; ν is the wave number; and T is the temperature. Assuming that near-surface layers of the atmospheric path and the substance have close temperatures, we can rewrite Eq. (1) in the form

$$B = \Phi_0 \tau_{atm} \tau_{sub} + P(1 - \tau_{atm} \tau_{sub}), \quad (2)$$

where $P = P(T_{eff}, \nu)$, T_{eff} is the effective temperature of the observation path. In this case, for the relative identification technique, the normalized spectrum of the substance can be determined from the following equation:

$$\tau_{sub}(\nu) = \frac{B(\nu) - P(T_{eff}, \nu)}{B_0(\nu) - P(T_{eff}, \nu)}, \quad (3)$$

where $B(\nu)$ is the spectrum of the observation path determined according to Eq. (1), $B_0(\nu)$ is the spectrum of the background surface with no pollutants in the atmosphere

$$B_0 = \Phi_0 \tau_{atm} + P_{atm}(1 - \tau_{atm}).$$

To perform the identification by a normalized spectrum (3) using the relative technique, it is necessary to record both the spectrum of the observation path $B(\nu)$ and the spectrum of the background surface with no pollutants in the atmosphere $B_0(\nu)$ [5].

Taking into account the additivity of the optical density and the exponential dependence of the transmission coefficient on the optical density [1], we can transform Eq. (2) to the form

$$B = \Phi_0 \tau_\Sigma + P(1 - \tau_\Sigma),$$
$$\tau_\Sigma(\nu) = \tau_{atm}(\nu)\tau_{sub}(\nu) = e^{-(D_{atm}(\nu) + D_{sub}(\nu))}, \quad (4)$$

where $\tau_\Sigma(\nu)$ is the total transmission coefficient containing signatures of all objects and substances on the observation path; $D_{atm}(\nu)$ and $D_{sub}(\nu)$ are the optical densities of the atmospheric path and the substance, respectively.

In [2], it is shown that many natural and artificial surfaces (clouds, trees, buildings) emit like a black body. Consequently, taking the spectrum of the background surface equal to the Planck function at some temperature T_0, we can transform Eq. (4) to the form

$$B(\nu) = P(T_0, \nu)\tau_\Sigma(\nu) + P(T_1, \nu)(1 - \tau_\Sigma(\nu)),$$

From here, we can find the dependence for the calculation of the total transmission spectrum of the observation path

$$\tau_\Sigma(\nu) = \frac{B(\nu) - P(T_1, \nu)}{P(T_0, \nu) - P(T_1, \nu)}. \quad (5)$$

Thus, the absolute model of substance identification assumes the recording of only the spectrum of the observation path, but the normalized spectrum (5) obtained in this way contains the signatures of all substances at the vision line.

To calculate the total transmission coefficient according to the absolute model, it is necessary to know the temperature of the background surface T_0 and the effective temperature of the observation path T_1, which are usually hard to measure. Consequently, it is necessary to adjust two Planck functions. For this purpose, the Planck function is modified as

$$P*(T, \nu) = (1 + c\nu)P(T + \Delta T, \nu), \quad (6)$$

where c and ΔT are the modification parameters variable in the given range. The parameter c is introduced for practical reasons and varies in the range [–0.5; 0.5]. The Planck functions are optimized so that one curve lies under the experimental spectrum, while the other lies above it. Thus, for example, to adjust the Planck function to the spectrum to the spectrum $B(\nu)$ from below, we must solve the equation

$$F(\Delta T) = \min_\nu [B(\nu) - (1 + c\nu)P(T + \Delta T, \nu)] = 0. \quad (7)$$

Equation (7) is solved by the zero-order method because function (7) is nondifferentiable. Once the optimization procedures were completed, we obtain two modified Planck functions and, after their substitution into Eq. (5), it is possible to calculate the total transmission spectrum of the observation path $\tau_\Sigma(\nu)$.

CALCULATION OF THE ATMOSPHERIC SPECTRUM

The total transmission spectrum of the observation path obtained in the previous section includes the signatures of all path objects, which significantly complicates the procedure for identifying the substance, especially in the clear-sky situation because, in this case, the signatures of atmospheric constituents (water vapor, ozone, etc.) are strong and suppress the signatures of the target substance. Therefore, it is necessary to calculate the atmospheric spectrum with the following sorting out the signatures of atmospheric constituents and the separation of the spectrum of a target substance.

Let us consider M spectra of atmospheric paths recorded under different conditions D^j, $j = 1, \ldots, M$, each of which is the sum of spectra of atmospheric gases H_2O, CO_2, O_3, NO_2, N_2O, etc. For a mixture of noninteracting gases, the following relation is valid [1]:

$$D^j = \sum_{i=1}^{N} D_i \alpha_i^j, \qquad (8)$$

where D^j is the jth spectrum of the atmospheric path; i is the number of an atmospheric gas; j is the number of an experimental atmospheric spectrum; N is the number of atmospheric gases; and α_i^j is the relative integral concentration, which is equal to the ratio of the current integral concentration to that for which the reference spectrum is obtained. To calculate the atmospheric spectrum, the following linear combination of the spectra of atmospheric gases from the database is used:

$$D_{atm} = \sum_{j=1}^{M} D^j \beta^j,$$

where $D_{atm} = D_{atm}(\nu)$ is the calculated atmospheric transmission spectrum, β^j are the proportionality coefficients, and M is the number of atmospheric spectra in the database. Below, we will show the possibility of obtaining the sum of the type (8) in the following form:

$$D_{atm} = \sum_{i=1}^{N} D_i \gamma_i,$$

where γ_i are the proportionality coefficients,

$$D_{atm} = \sum_{j=1}^{M} \beta^j \sum_{i=1}^{N} D_i \alpha_i^j = \sum_{j=1}^{M} \sum_{i=1}^{N} \beta^j D_i \alpha_i^j$$

$$= \sum_{i=1}^{N} D_i \sum_{j=1}^{M} \beta^j \alpha_i^j = \sum_{i=1}^{N} D_i \gamma_i.$$

Thus, the proportionality coefficients of the optical densities have the form

$$\gamma_i = \sum_{j=1}^{M} \beta^j \alpha_i^j. \qquad (9)$$

In the matrix form, Eq. (9) can be rewritten as

$$\Gamma = BA. \qquad (10)$$

The sought set of the parameters has the form

$$B = \Gamma A^{-1}.$$

For the spectrum of any atmospheric path to be modeled from a set of earlier recorded spectra (that is, for any matrix Γ, there is a solution of Eq. (10)), it is necessary that an inverse matrix A^{-1} would exist. Thus, to model an atmospheric spectrum from previously recorded spectra, it is necessary to have a sufficient or excessive set of linearly independent spectra of atmospheric paths.

For this purpose, we have compiled a database of normalized spectra of atmospheric paths recorded under different conditions and spectra of broadband atmospheric constituents (for example, ozone) calculated based on the HITRAN database [3], which are only slightly affected by the FTSR apodization. To construct an atmospheric spectrum using the atmospheric database, the functional of the following form is constructed:

$$\Phi(Z)$$

$$= \int_{\nu_{min}}^{\nu_{max}} ((\delta(Z,\nu))^2 + e^{-\alpha \delta(Z,\nu)}) w_{\tau_\Sigma}(\nu) d\nu \longrightarrow \min, \qquad (11)$$

$$\delta(Z,\nu) = e^{-\sum_{k=1}^{M} z_k D_k(\nu)} - \tau_\Sigma(\nu), \qquad (12)$$

where $\delta(Z, \nu)$ is the discrepancy, α is the weighting coefficient of the penalty function determined from practical reasons; M is the number of database spectra used in the functional optimization, Z are the relative integral concentrations, and $w_{\tau_\Sigma}(\nu)$ is the weighting function. The weighting function is normalized to unity and represents the spectral error

$$w_{\tau_\Sigma}(\nu) = 1/\sigma_{\tau_\Sigma}^2(\nu), \qquad (13)$$
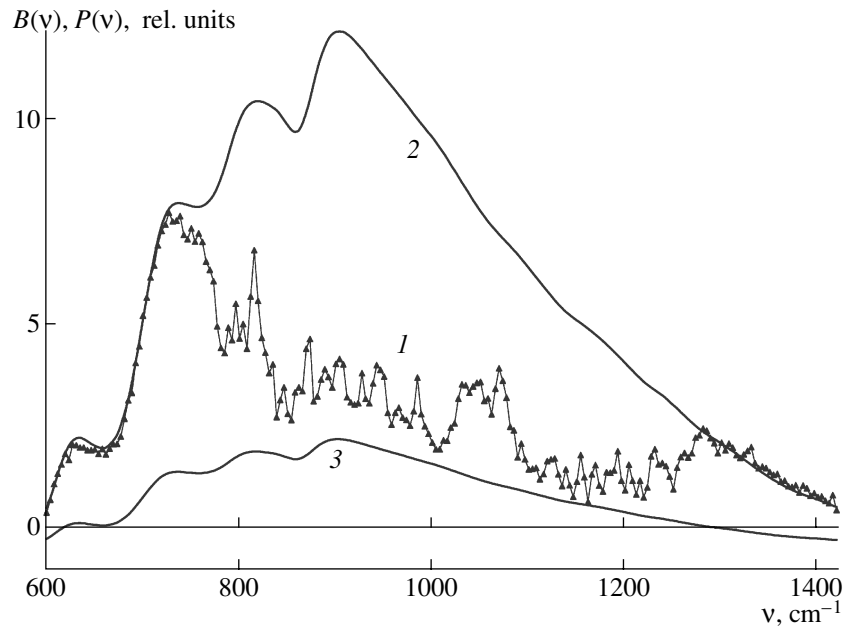
Fig. 1. Procedure for modifying two Planck functions. All spectra are shown in relative units taking into account the FTSR transmission function: (curve *1*) experimental spectrum, (*2* and *3*) Planck functions constructed at different temperatures and modification coefficients *c*.
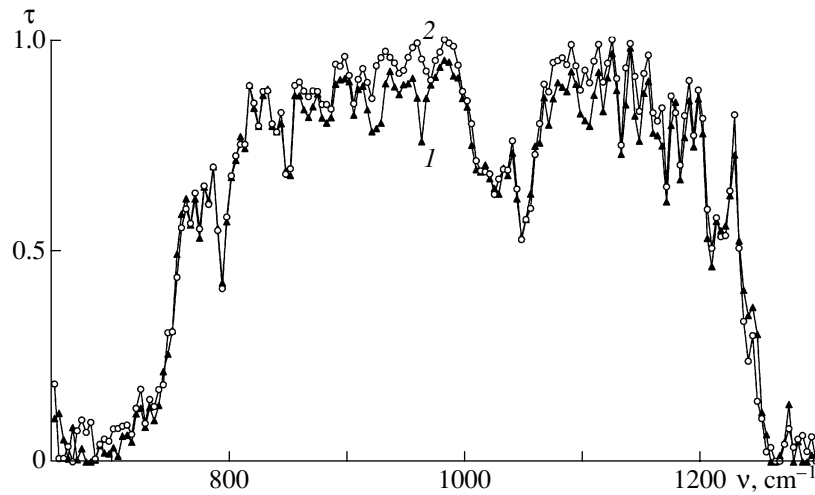
Fig. 2. (*1*) Transmission spectrum of the clear atmosphere calculated based on (*2*) the total transmission spectrum and the atmospheric database.

where $\sigma^2_{\tau_\Sigma}(\nu)$ is the variance of the spectral error, which is determined as the error of indirect measurements as follows:

$$\sigma^2_{\tau_\Sigma} = \left(\frac{\partial \tau_\Sigma}{\partial B}\right)^2 \sigma^2_B.$$

Here, σ^2_B = const is the variance of the spectral error in a recorded spectrum. In Eq. (11), the first term is the

squared discrepancy (12) of two spectra and the second term is the penalty function, which allows the optimization to be performed at the given limited set of values:

$$e^{-\sum_{k=1}^{M} z_k D_k(\nu)} \geq \tau_\Sigma(\nu), \quad (\nu_{min} + \delta_{min}, \nu_{max} - \delta_{max}),$$

which does not allow the atmospheric spectrum to suppress the substance signatures upon subsequent sorting-
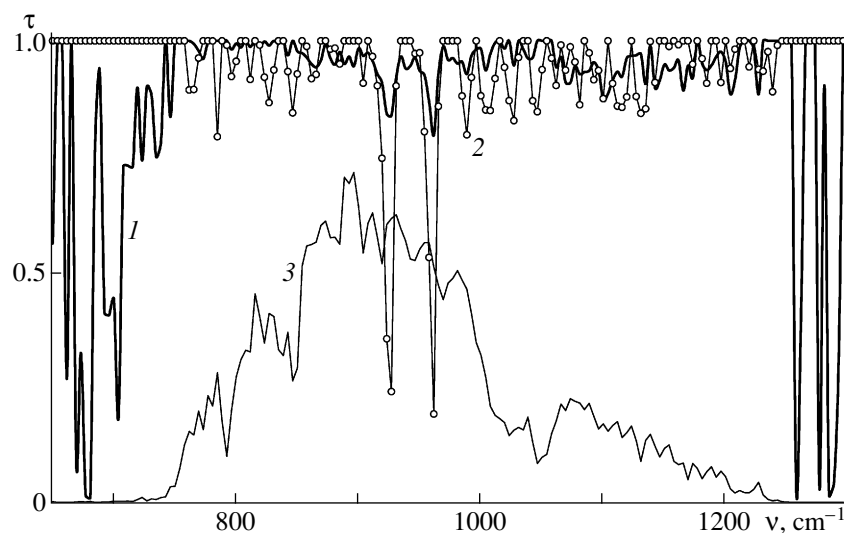
Fig. 3. Procedure of substance identification: (curve *1*) spectrum of a substance separated at the previous stages, (*2*) reference spectrum of ammonia from the database, and (*3*) weighting function.
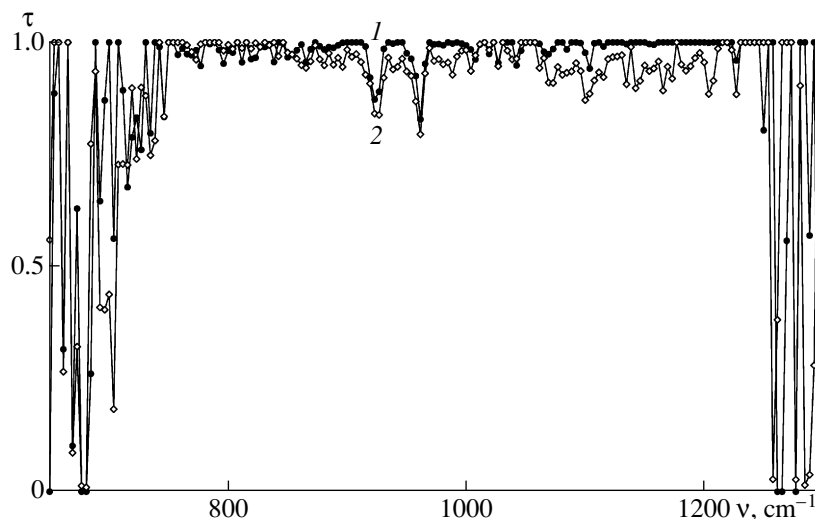
Fig. 4. Ammonia transmission spectra obtained by two different techniques: (curve *1*) spectrum obtained after processing of a single spectrum by the absolute technique, (*2*) spectrum obtained by the relative technique of substance identification.

out of this spectrum according to the equation

$$\tau_{sub}(\nu) = \tau_{\Sigma}(\nu)/e^{-\sum\limits_{k=1}^{M} z_k D_k(\nu)}, \quad \tau_{sub}(\nu) \in [0, 1]. \quad (14)$$

Since the functional (11) is differentiable with respect to Z, the gradient descent method is applied for optimization.

SUBSTANCE IDENTIFICATION

The normalized spectrum of a substance obtained according to Eq. (14) passes the last stage of the analy-sis [1, 5], which first involves the identification of the substance, followed by quantitative analysis using regression methods. At the previous stage, the correla-tions of spectra (transmission coefficients) of database substances are calculated. The database substance for which the correlation coefficient is the highest and exceeds some preset threshold is believed to have been detected in this experiment. Then, a quantitative analy-sis is performed, which yields the integral concentra-tion of the found substance by minimizing the discrep-ancy functional.

TESTING

The described absolute technique is implemented as a software package, which allows one to perform qualitative and quantitative analysess of substances based on an input interferogram or a spectrum. Measurements are conducted on an FTSR with a spectral resolution of 8 cm^{-1} in a range of 600–1400 cm^{-1}. The technique has been tested in identification experiments both for substances with broad bands and lines in the spectrum (lavsan, polystyrene), which simplifies the identification problem, and for substances with narrow lines and bands (ammonia), which are usually overlapped by the atmospheric spectrum (ethanol, fluoroplastic). Positive results of the identification of different types of substances have been obtained for various weather conditions. All stages of the spectral analysis are illustrated using the ammonia vapor in the open atmosphere as an example. The ammonia spectrum was recorded in summer at an air temperature of 20°C against the clear sky at an elevation angle of the vision line of 50°. Figure 1 illustrates the procedure of construction of two Planck functions, after which the total transmission coefficient is separated. At the following stage (Fig. 2), the total transmission coefficient is used to construct the atmospheric spectrum, which is then subtracted from the total spectrum with the separation of the transmission spectrum of the substance (Fig. 3). At the last stage, the substance is identified by its spectrum. Figure 4 illustrates the substance spectra obtained with the aid of the technique of analysis of a single FTSR interferogram (the absolute technique) and the technique requiring the recording of the total spectrum of the observation path and the spectrum of the background surface in the clear atmosphere without pollutants (the relative technique) [1, 5, 6]. In both cases, substances have been identified and the integral concentrations have been calculated. With the use of the relative technique of the analysis, the correlation and the integral concentration are equal to 0.80 and 91.21 mg/m^2, while, for the absolute technique, the correlation and the integral concentration for ammonia are 0.71 and 122.52 mg/m^2, respectively. The relative error of determination of the integral concentrations for the two techniques does not exceed 30%, which is acceptable for gas-analytic systems [1] and indicates that the absolute technique can be used for the qualitative and quantitative analysis of substances in the open atmosphere.

CONCLUSIONS

The experimental technique and the algorithm for the qualitative and quantitative analysis of substances in the open atmosphere from the results of processing of a single Fourier-transform spectroradiometer interferogram have been proposed. The proposed technique was implemented as a software package and was tested in the processing of results of field measurements. Positive substance identification results are obtained for substances having both broadband and narrowband spectra recorded against the background of different background surfaces and under various weather conditions. With the spectrum of ammonia recorded against the clear sky taken as an example, the absolute and relative techniques have been analyzed comparatively. The relative error in this case is no higher than 30%, which indicates that the described technique can be used for the qualitative and quantitative analysis of substances in the open atmosphere.

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SPELL: 1. analysess