

Selection of optimal analytical line at interference of spectra of gases to be detected

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A method is presented for comparative analysis of absorption line properties in the case of interference between rotation-vibration bands of the gas to be detected and a foreign gas. It can be applied to high-sensitivity analysis of complex gas mixtures, when detection of a weak analytical line is hampered by closely located more intense interfering lines of foreign gases. Disappearance of analytical line extremes in the studied spectrum is proposed to be used as a criterion of assessment. The concentration ratio of the analyzed and foreign gases can be used for quantitative analysis and comparison of properties if this criterion is fulfilled. The criterion can be applied to the first and second derivatives of the absorption spectra as well. Equations are obtained that relate line parameters to concentrations of the detected and foreign gases, at which analytical line extremes disappear from the absorption spectrum. The relationship is found between the concentration of the detected gas under this condition and its first and second derivatives, as well as the dependence of the conditions of extreme disappearance on the total pressure of the gas mixture.

Introduction

Optimal selection of spectral lines for gas analysis is extremely urgent to improve the sensitivity of measurements. Current spectral methods allow changes in the optical density due to absorption to be detected at the level of 10^{-7} (Refs. 1–3), what corresponds to the concentration sensitivity $\sim 10^{-10}$ vol.% for some gaseous molecules. In analyzing gases at trace concentrations with such sensitivity in gas mixtures, the problem of interference (overlap) of rotational-vibrational (RV) absorption spectra of detected and foreign substances arises. Accidental coincidence of line centers or their masking at overlap becomes the main factor restricting the sensitivity of analysis. This is especially important in analysis of atmospheric or expired air because of high content of H_2O , CO_2 , and some other gases. Since the content of these gases may exceed by 6–8 orders of magnitude the content of analyzed substances, even relatively weak lines of foreign gases can hinder the detection.

Analysis of positions and characteristics of lines in the RV bands of detected and foreign gases allows us to assess the effect of interference in different spectral ranges and to tune an analyzer for operation in the most favorable range. For such analysis, we should have the criterion for comparison of the various positions of weak analytical lines among more intense interfering lines. This criterion should give us the possibility of estimating the level of analyzed concentrations, at which the interference becomes significant. This will allow justified selection of not only analytical lines, but also the methods and conditions of their recording, for example, the use of

differential methods, operation in the open atmosphere or in a pumped cell.

In this paper, we propose a method for solution of the above problem. For a comparison of analytical properties of the lines, a criterion is suggested close, in essence, to the criterion of resolution of two spectral lines having the same intensity, which is applied to estimate the resolution of spectral devices.⁴ In the latter case, two close spectral lines are thought resolved, if a dip is observed at the center of their net profile. In the case of significant (some orders of magnitude) difference in the line intensity, it is proposed to analyze the behavior of extremes of the net spectrum. Since most problems of gas analysis are solved at the atmospheric pressure, this criterion is applicable to lines having the Lorentz profile. This allows line parameters to be related analytically to the concentrations of the studied and foreign substances, the conditions and methods of recording spectra to be taken into account, compared, and optimized.

Disappearance of analytical line extremes

Usually, to determine the concentration of a substance of interest from the transmission spectrum of a medium studied, resonance features specific for this substance, for example, individual lines of the RV structure, are used. If a weak analytical line lies on a slope of a more intense one, then the contrast of the used resonance feature decreases as the absorption in the weak line decreases or lines approach each other (Fig. 1).

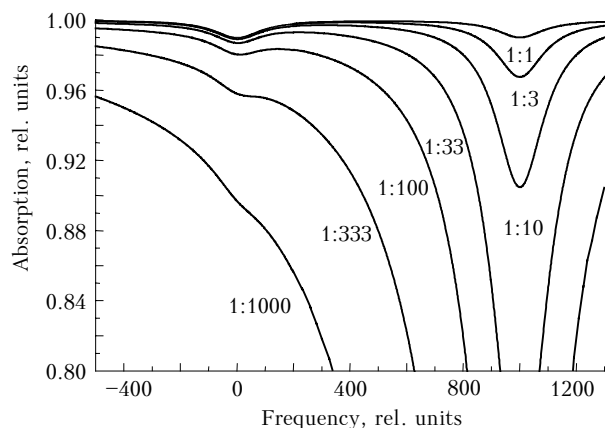


Fig. 1. Evolution of the net transmission spectrum of two Lorentz-shaped lines of the same width at changing the absorption intensity ratio between them. The separation between line centers 10 times exceeds their halfwidths Δ (FWHM).

In the limit, the resonance absorption in the weak line becomes almost indistinguishable, and the line itself becomes unfit for concentration measurements.

In the evolution of the net absorption profile of such lines with changing relative content of substances, we can separate the disappearance of analytical line extremes (DALE). This point corresponds to a certain absorption ratio between the analytical and interfering lines. The value of this ratio is determined by the line intensity, width, the separation between the lines, and the gas concentrations. For example (see Fig. 1), for lines of equal width and intensity separated by five full widths, DALE occurs at the concentration ratio $\sim 1:333$. Because the DALE point is unique for every pair of lines, it is proposed to use it to characterize parameters of this pair and as a criterion to assess analytical properties of the considered absorption line of the detected substance under conditions of interference with the interfering line.

DALE at direct recording of absorption spectrum

Let us consider in detail the DALE point for two close lines at direct recording of absorption spectrum under conditions typical of microanalysis of complex gas mixtures, for example, atmospheric or expired air.

1. An absorption line is described by the Lorentz profile:

$$\kappa(\nu) = Sf(\nu) = S \frac{1}{\pi} \frac{\Delta}{\Delta^2 + \nu^2},$$

where S is the line intensity; f is its form factor.

2. The optical density at the center of the interfering line A_i is much higher than A_a for the analytical line, that is,

$$A_a = S_a c_a L f_a(0) \gg A_i = S_i c_i L f_i(0),$$

where the subscripts a and i stand for the analytical and interfering substances; c is the gas concentration; L is the optical path length.

3. In the spectral range under consideration, $A_i \ll 1$, and this allows us to restrict our consideration to analysis of only absorption spectra.

4. The relative concentrations of the analyzed and interfering substances in the gas mixture under study are much lower than unity, therefore the collisional broadening of lines is determined by other components of the mixture.

Consider the relation between the parameters of the analytical and interfering lines when extremes caused by the analytical line disappear in the net spectrum of the optical density

$$\tau_S(\nu) = \tau_a(\nu) + \tau_i(\nu - \delta)$$

(δ is the separation between line centers).

If lines are separated widely enough, then the net profile has, besides the maximum corresponding to the center of the interfering absorption line, two other extremes: minimum and maximum (see Fig. 1). As the separation between the lines decreases, these two extremes become closer and then disappear after merging. In the spectrum of the derivative $\tau'_S(\nu)$, the presence of extremes corresponds to intersection with the abscissa (Fig. 2).

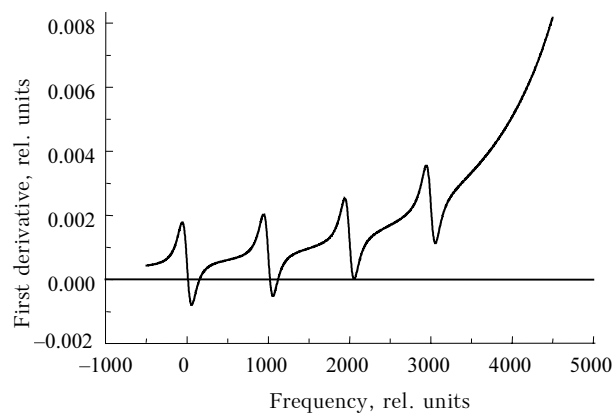


Fig. 2. First derivative of the net absorption spectrum of four weak Lorentz lines at the wing of the intense line (intensity ratio of 1:5000); all the five lines have the same width.

The derivative of the analytical line giving no extremes does not intersect the abscissa. Thus, DALE occurs at such separation between the analytical and interfering lines that $\tau'_S(\nu) = 0$, and $\tau'_a(\nu)$ takes its minimum value (analytical line to the left from the interfering one). For the Lorentz profile, the minimum of the first derivative is to the right from its center at the distance $\Delta\nu = \Delta_a/\sqrt{3}$ and takes the value

$$\tau'_{a \min} = -\frac{9}{8\sqrt{3}} \frac{A_a}{\Delta_a}.$$

At the same time, for the first derivative of the interfering line profile, the following approximate equality

$$\tau'_i(v) \approx -2A_i \Delta_i^2 / v^3$$

is fulfilled at a rather large distance from its center, that is, at $|\Delta v| \gg \Delta_i$.

Equating the last two equations, we can find the relation of the distance between the centers of the considered lines to their amplitudes and DALE point:

$$\delta_0 \approx \frac{2}{\sqrt{3}} \sqrt[3]{2\Delta_i^2 \Delta_a \frac{A_i}{A_a} + \frac{\Delta_a}{\sqrt{3}}}. \quad (1)$$

If $A_i \gg A_a$ and $\Delta_a \approx \Delta_i = \Delta$, then, neglecting the second term in Eq. (1), we obtain that at direct spectrum recording the parameters of the analytical and interfering lines of the same width at the DALE point are related as

$$\delta_0 \approx \frac{2\Delta}{\sqrt{3}} \sqrt[3]{2 \frac{A_i}{A_a}} \approx 1.46 \Delta \sqrt[3]{\frac{A_i}{A_a}}.$$

DALE for the first and second derivatives of the absorption spectrum

To improve the sensitivity of recording the resonance absorption, in particular, with tunable diode lasers, detection of the first or second derivative of the absorption spectrum is used. Along with filtering the low-frequency noise out of the useful component of the signal and increasing the contrast of resonance features of the spectrum, differentiation changes the concentration ratio, at which DALE occurs for the closely spaced analytical and interfering lines, and improves the conditions of detection of the analyzed substance against the background of strong resonance absorption.

The separation between the centers of two Lorentz lines, at which the extremes in the first and second derivatives of the net spectrum disappear (Figs. 3 and 4), can be found in a similar way. The first derivative of the Lorentz profile changes most quickly at the point $v = 0$ (see Fig. 3), corresponding to the minimum of its second derivative. For the analytical line at this point we have

$$\tau''_{a \min} = -2 A_a / \Delta_a^2.$$

At the far wing of the second derivative of the interfering line

$$\tau''_i(v) \approx 6 A_i \Delta_i^2 / v^4.$$

The separation between the analytical and interfering lines, at which $\tau''_i(v) = \tau''_{a \min}(v)$, that is, the extreme of the first derivative of the analytical line disappears, is determined as follows:

$$\delta_1 \approx \sqrt[4]{3\Delta_i^2 \Delta_a^2 \frac{A_i}{A_a}} \approx 1.3 \sqrt[4]{\Delta_i^2 \Delta_a^2 \frac{A_i}{A_a}}. \quad (2)$$

At $\Delta_a \approx \Delta_i = \Delta$ this equation can be reduced to a simpler one:

$$\delta_1 \approx 1.3 \Delta \sqrt[4]{A_i / A_a}.$$

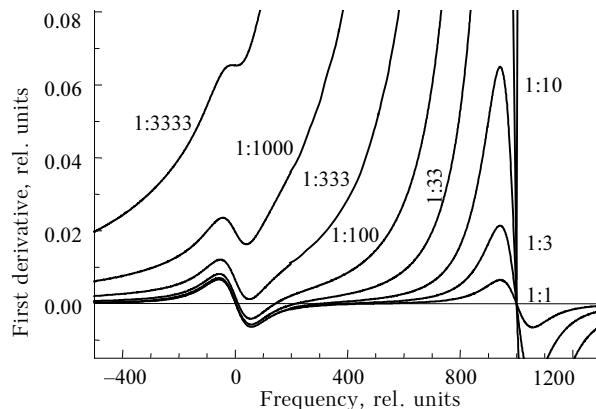


Fig. 3. Evolution of the first derivative of the net profile of two Lorentz lines having the same width at the varying intensity of the interfering line, $\delta = 10\Delta$.

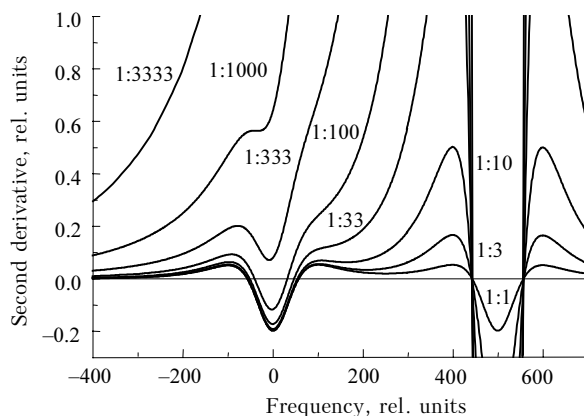


Fig. 4. Evolution of the second derivative of the net profile of two Lorentz lines having the same width at the varying intensity of the interfering line, $\delta = 5\Delta$.

By analogy and with the allowance for the fact that the smallest extreme of the second derivative of the Lorentz line lies to the left from its center (see Fig. 4), the separation between the line centers for DALE in the second derivative can be determined as

$$\delta_2 = \sqrt[5]{\frac{A_i}{A_a} \Delta_i^2 \Delta_a^3 \frac{(1 - 1/\sqrt{5}) 8\sqrt{5}}{\sqrt{1 - 2/\sqrt{5}}}} - \Delta_a \sqrt{1 - 2/\sqrt{5}} \approx 1.38 \sqrt[5]{\Delta_i^2 \Delta_a^3 \frac{A_i}{A_a}} - 0.32\Delta_a. \quad (3)$$

At $A_i \gg A_a$ and $\Delta_a \approx \Delta_i = \Delta$ we have

$$\delta_2 \approx 1.38 \Delta \sqrt[5]{A_i / A_a}.$$

Thus, at detection by use of the first and second derivatives of the absorption spectrum of two close lines, their parameters at the DALE point are connected by Eqs. (2) and (3), respectively.

Relation between concentrations at DALE

The use of Eqs. (1)–(3) is convenient for estimating relative concentration of the analyzed substance in a gas mixture at the DALE point (hereinafter this concentration is referred to as the critical one). For such an estimation, it is sufficient to have tabulated data on the parameters of absorption lines of the detected and interfering substances, including their positions, intensities, and pressure-induced broadening coefficients. It is convenient to estimate the critical concentration relative to the content of the interfering substance, whose concentration in the analyzed gas mixture is usually known and rather stable. Such analysis is useful, for example, for selecting the analytical line for detection of trace concentrations of some gaseous substance in the atmospheric or expired air, in which water vapor or CO₂ can serve interfering substances.

Using the relation of the optical density with the concentration and line intensity, from Eqs. (1)–(3) we can obtain the equations relating the sought critical concentration of the analyzed substance to the concentration of the interfering substance for different methods of the absorption spectra recording. In the case of direct recording, the critical concentration can be determined as

$$c_a^{(0)} \approx 3.11 \frac{\Delta_a \Delta_i^2}{S_a \delta^3} S_i c_i. \quad (4)$$

Similarly, for the first and second derivatives of the signal

$$c_a^{(1)} \approx 2.86 \frac{\Delta_a^2 \Delta_i^2}{S_a \delta^4} S_i c_i, \quad (5)$$

$$c_a^{(2)} \approx 5 \frac{\Delta_a^3 \Delta_i^2}{S_a \delta^5} S_i c_i. \quad (6)$$

It follows from Eqs. (4)–(6) that the critical concentration of the analyzed substance is linearly proportional to the line intensity and the concentration of the interfering substance and, thus, the higher are these parameters, the less sensitive is detection. On the contrary, the stronger is the analytical line used the lower is the detection limit. Besides, it is worth noting the inverse power dependence of the critical concentration on the separation between the centers of the considered lines. This dependence means that, from the viewpoint of selection of the optimal analytical line, the distance to the center of the interfering line is a far more critical factor than the intensity ratio. The

higher is the degree of differentiation, the more significant is the role of the separation between the lines.

Based on Eqs. (4)–(6), we can also find the relation between the critical concentrations for different methods of spectrum recording. In particular:

$$c_a^{(1)} \approx 0.92 \frac{\Delta_a}{\delta} c_a^{(0)},$$

$$c_a^{(2)} \approx 1.61 \left(\frac{\Delta_a}{\delta}\right)^2 c_a^{(0)}.$$

Thus, every next differentiation of the spectrum decreases the threshold of influence of the interfering line proportionally to the ratio of the analytical line FWHM to the separation between the lines. These equations not only demonstrate that the increase in contrast of the detected signal due to differentiation of absorption spectra leads to the increase in the gas detection sensitivity, but also allow one to predict the magnitude of the effect. It should be noted that the efficiency of improving the conditions for analysis depends only on the width of the analytical line and the distance to the interfering line.

Effect of decrease in the total pressure of the analyzed gas mixture

Another method to increase the contrast of the analytical absorption spectrum under conditions of low relative concentrations of the analyzed and interfering substances is the decrease of the total pressure of the gas mixture analyzed. It is based on the fact that in the case of prevalence of line broadening due to collision with foreign gases, the decrease in the total pressure leads to only line narrowing, leaving the level of the optical density at the line center unchanged. This effect is observed in a wide range of the total pressure, where the absorption line is described by the Lorentz profile. From below, this range is limited by the gradual transition from the Lorentz profile to the Doppler one, and from above – by the possible effects of spectral interference of lines at their overlap. At the spectral analysis of atmospheric or expired air with the use of an analytical cell, we can decrease the total pressure by an order of magnitude (from roughly 760 to 70 mm Hg), remaining under conditions of prevalence of collisional broadening.

Consider the dependence of critical concentrations on the total pressure of gas mixture at different methods of recording the absorption spectrum. Taking into account that under conditions of dominant pressure of foreign gases the line width is directly proportional to the total pressure P of the gas mixture, Eqs. (4)–(6) can be transformed to the following form:

$$c_a^{(0)}(P) \approx 3.11 \frac{\gamma_a \gamma_i^2 S_i}{S_a \delta^3} c_i P^3,$$

$$c_a^{(1)}(P) \approx 2.86 \frac{\gamma_a^2}{S_a} \frac{\gamma_i^2 S_i}{\delta^4} c_i P^4,$$

$$c_a^{(2)}(P) \approx 5 \frac{\gamma_a^3}{S_a} \frac{\gamma_i^2 S_i}{\delta^5} c_i P^5,$$

where γ_a and γ_i are the coefficients of collisional broadening by foreign gases for the analytical and interfering lines, respectively.

The latter three equations demonstrate high efficiency of using a decrease in the total pressure of the analyzed gas mixture for improving the detection conditions in the case of weak resonance absorption. At direct detection, the transition from the atmospheric pressure to the total pressure ~70 mm Hg can yield a three orders gain in lowering the detectable concentration. When using the second derivative, the same decrease yield the five orders of magnitude gain.

Conclusion

Thus, it is shown that the criterion based on DALE point in the spectrum of the analyzed gas mixture can be used at selection of the optimal analytical line for comparison of line characteristics. This criterion is applicable in the case that the main restricting factor is interference of RV bands of the analyzed and interfering substances. For Lorentz lines, their parameters under the DALE conditions are related by simple analytical equations allowing determination of the critical concentration of the analyzed substance, below which resonance features can hardly be detected by ordinary methods. This approach is also applicable

in the case of recording the first and second derivatives of the absorption spectrum, and in every particular case, it can be used to determine the efficiency of differentiation of the recorded spectra as a measure aimed at increasing the detection sensitivity based only on known spectral parameters of the analytical line. In this way, we can estimate the degree of improvement of the conditions for recording a weak line due to the increase of the absorption spectrum contrast at a decrease of the total pressure of the gas mixture analyzed.

The criterion proposed allows selection of the optimal analytical line to be easily automated for analysis of the absorption line of the studied substance in a complex gas mixture by use of data from spectral atlases like HITRAN-96 (Refs. 5 and 6) for comparison of analytical characteristics.

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