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Analytical capabilities of a thermodesorption spectrometer with a surface-ionization detection of organic molecules in air

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This paper presents the results of research on the development of a mathematical model of thermal desorption spectrometry with a surface ionization method for detecting molecules of organic substances, as well as an analysis of the capabilities of a thermal desorption spectrometer operating on the basis of this method. The mathematical model of the method was developed on the basis of the regularities of thermal desorption spectrometry, as well as the regularities of surface ionization of molecules of organic substances under non-stationary conditions. The spectrometer consists of a surface ionization detector and an evaporator of substances heated in a thermally programmed mode. The adjustment and selection of the operating mode of the spectrometer were carried out on the basis of the mathematical model of the method. The analytical capabilities of the spectrometer were studied by comparing the thermodesorption spectra of a mixture of chromatographically pure cannabinoids and an extract of the biological fluids of a marijuana user (blood, urine), as well as the spectra of chromatographically pure morphine and urine extracts of a heroin user. The results of the analysis showed the perspectives of the proposed method and instrument for the detection and analysis of drugs and psychotropic drugs in extracts of biomaterials of consumers of these substances without chromatographic separation.

Keywords: biosamples of drug users, mathematical model of the method, thermal desorption spectrum, identification and quantitative analysis.

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Introduction

By their nature the active organic compounds (AOCs) are low-volatile and thermally unstable compounds; as a result, in spectrometric studies of AOCs the information obtained depends both on the ionization method used and on their physicochemical nature. At present, various methods of ionization of AOC molecules are used for laboratory analyzes — ionization by field, by electrons, by photons, ionization by a beam of accelerated ions and atoms, chemical and spray methods of ionization [1–9]. Together with various methods of mixtures separation and methods of ions separation, they make it possible to carry out qualitative and quantitative analyzes of complex mixtures, including biosolutions [10–15]. By now, reference data and electronic bank of mass spectra of AOC reference samples were created [16,17].

However, despite the high level of development of methods and instruments for the laboratory analysis of low-volatile active organic compounds, highly sensitive express direct (selective) analysis of samples in the field conditions remains one of the important directions in the analytical field development [18]. One of the main tasks of this direction is the creation of relatively simple and not requiring special conditions (gases, vacuum, etc.) devices with small dimensions, energy consumption and analysis time, which will decrease the cost of devices and sample analysis. At present, numerous scientific and scientific-technical works are being carried out relating this discipline [19–33]. These include works on the use of the phenomenon of surface ionization (SI) of organic compound molecules in the analysis of AOC in complex multicomponent biosamples without chromatographic separation [26–33].

One of the important features of SI-based detectors is their operability in various gas-phase media, including air, as well as high efficiency and unique selectivity to nitrogen base AOCs, which made it possible to develop highly sensitive and highly selective methods and devices that operate both in vacuum conditions, and in air [25–26,28,30–33]).

Thanks to the successes achieved in gas analysis devices engineering based on the SI phenomenon, it attracts attention both to the basis for the development of new methods and the creation of ecologically friendly, simple, relatively inexpensive, selective and highly sensitive portable devices.

One of the possible ways to solve the actual problem of the analytical field of creating promising devices for express out-of-laboratory analysis of AOC [18,25] is SI development of for gas analytical devices engineering. It was further developed in the form of a spectrometer using the principle of thermodesorption spectrometry [34] — of temperature-programmed evaporation (desorption) of

analyte molecules with their subsequent registration in air flow by SI detector [35], which can potentially serve as a prototype of a portable device.

The purpose of this paper is to demonstrate the capabilities of a thermodesorption (TD) spectrometer — surface ionization gas analyzer during the analysis and check of AOC when operating in air in specific studies to determine TD and SI characteristics of AOC molecules and non-specific studies — to detect and analyze AOC in various objects, including extracts of biosolutions.

1. Method and experimental technique of study

The diagram of the system of analyte molecules evaporator and SI detector of the spectrometer is shown in Fig. 1 [35]. Here, iridium-alloyed molybdenum oxide was used as the emitter, made as a hollow cylinder 12 mm long and 2.5 mm in diameter. T_E of the emitter was measured with a chromel-alumel thermocouple soldered to 1/4 of its length. The work T_E of the emitter is 670 K. The evaporator is a graphitized metal cup 3 mm in diameter and 1.5 mm high, the temperature of which is also measured with a chromel-alumel thermocouple. Its heating $T(t)$ was relative to temperature $T_0 = 300 \pm 2$ K with a linear rate $\omega = 10°$C/s. The ion current $I_s(T)$ is recorded synchronously with the spectrometer software „Druggy“ version 1A. „Druggy“–1A“ program determines the ion current, the area under the spectrum (in coulombs), and the temperature of the spectrum maximum. The program is equipped with an electronic database of TD spectra with calibration graphs. Up to ten TD spectra are compared by the operator in the software environment, and substances are identified by maximum temperatures, and quantitative analysis is performed using calibration curves.

The experiments used chromatographically pure samples of morphine (at least 99%) and a mixture of cannabinoids (at least 99%) — delta-9-tetrahydrocannabinol (Δ^9-THC), cannabidiol (CBD) and cannabinol (CBN) in proportions of 100, 50 and 50 ng respectively, an extract of a natural № 1320 cannabis sample, as well as extracted biological samples of heroin and cannabis users. An extract of the natural cannabis sample, as well as extracted biological samples (blood and urine) were presented by the Laboratory of Legal Chemistry of the Republican Office of the Chief Medical Examiner of the Ministry of Health of the Republic of Uzbekistan.

The mathematical model of the method proposed in this paper was developed by integrating the objective laws of TD spectrometry and the objective laws of SI of organic substance molecules under nonstationary conditions. Numerical analyzes were carried out in the Wolfram Mathematica software. The analytical capabilities of the spectrometer were studied by comparing TD spectra of the mixture of chromatographically pure cannabinoids and extract of the urine and blood of the cannabis user, as well as the spectra of chromatographically pure morphine and the extract of the urine of heroin users.

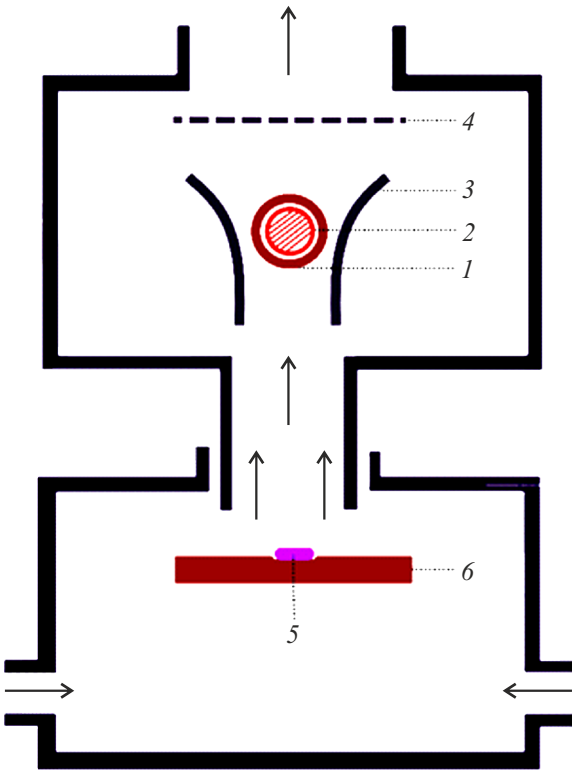

Figure 1. Diagram of evaporator with SI detector [35]: *1* — emitter; *2* — emitter heater; *3* — pulling electrode; *4* — ion collector; *5* — sample for analysis; *6* — evaporator.

2. Mathematical model of the method and TD spectrometer operation mode

When the evaporator is heated at a linear rate ω, the process of substance molecules evaporation is activated according to the behavior laws of TD spectrometry. On the surface of SI emitter

$$\nu_a = \eta\nu_{is} = -\eta\omega\frac{dn}{dT} = \eta V n \approx \eta V n_0 \times \exp\left[-\frac{RT^2}{\omega q} D \exp\left[-\frac{q}{RT}\right]\right] \quad (1)$$

part of the flow ν_a (1) of evaporating molecules ν_{is} from the evaporator is adsorbed, where $\eta = \frac{m_0 - m_p}{m_0}$ — substance utilization factor, in which m_0 — mass of the substance applied to the surface of the evaporator, m_p — lost mass of evaporated molecules of substances during analysis, q and V — heat and rate of evaporation (or sublimation) of substance molecules, D — constant; R — universal gas constant, n_0 — number of substance molecules deposited on the evaporator surface, n — number of substance molecules at time t.

Molecules adsorbed on the hot surface of the emitter can undergo heterogeneous chemical reactions of dissociation, dehydrogenation, association, or are desorbed in the initial state. At that, the number of molecules in adsorption states N, the number of particles of chemical reaction products N_i and molecules desorbing in initial states N_M, and the total number of desorbed particles N_s vary with the rate:

$$\frac{dN}{dT} = \eta\nu_{is} - \frac{AN}{\omega}, \quad \frac{dN_i}{dT} = \frac{\gamma_i AN}{\omega} - \frac{K_i N_i}{\omega}$$

and

$$\frac{dN_M}{dT} = \frac{\gamma_M AN}{\omega} - \frac{K_M N_M}{\omega}, \tag{2}$$

$$\frac{dN_s}{dT} = \frac{AN}{\omega} - \frac{K_M N_M}{\omega} = \sum_z \frac{K_i N_i}{\omega}, \tag{3}$$

where $A = K_M + \sum\limits_z K_i^d$ — the rate of loss of molecules in the adsorbed state, K_i^d – rate of heterogeneous chemical reactions of substance molecules in the i-th channel on the emitter surface, K_M — rate of thermodesorption of substance molecules in the initial molecular state from the emitter surface, z — number of channels of chemical reactions of molecules, $\gamma_i(T_E) = K_i^d/A$ — coefficient that determines the proportion of adsorbed molecules, which due to exposure to heterogeneous chemical reactions via i-th channel are converted into particles of i-th type, $\gamma_M(T_E) = 1 - \sum\limits_z \gamma_I(T_E)$ — the coefficient that determines the proportion of adsorbed molecules that are desorbed in the initial molecular state, K_i — the rate of desorption of i-type particles from the emitter surface.

The operating mode of the spectrometer is determined by the operating mode of the SI detector of the spectrometer (the operating mode of SI detectors is studied in detail in [36]). The first mode can be called the high-speed mode of the SI detector, in which the temperature of the maximum $T_{\max}$ of the substances spectra will not depend on the temperature T_E of the emitter, and the dependence of the ion current $I_s(t)$ registered by the SI detector will repeat the dependences of TD spectrometry. The second mode is called the low speed SI detector mode. In this mode, the temperature of the maximum $T_{\max}$ of the substances spectra and the dependence of the current of ions $I_s(t)$ recorded by the SI detector are function of the temperature T_E of the emitter. The dependence $I_s(t)$ will be shifted relative to the dependence of the flow of $\nu_a(t)$ molecules directed to the SI detector to the region of high temperatures of the evaporator. The dependence of the value $T_{\max}$ of spectra and $I_s(t)$ dependences on T_E are due to the dependence of the kinetic parameters of heterogeneous processes, such as K_i^d, K_i and K_M on T_E according to the law

$$K_i^d = G_i \exp[-E_i^d/kT_E], \; K_M = C_M \exp[-E_M/kT_E]$$

and

$$K_i = K_i^+ + K_i^0 = D_i \exp[-E_i^+/kT_E] + C_i \exp[-E_i^0/kT_E],$$

where T_E — emitter temperature, E_i, E_M and E_i — activation energy of the corresponding processes, G_i, C_M and C_i — pre-exponential factors.

The solutions of equations (2) and (3) will depend on the operation mode of the SI detector. In the high-speed mode of SI detector the rate of heterogeneous processes K_i^d, K_i and K_M occurring on the emitter surface will be high. In this case, the time interval between the adsorption of molecules on the emitter surface and the ionized particles desorption from it, as well as the rate of change in the number of particles (2) and (3) will be insignificantly small. And the solution of equations (2) and (3) for the current of ionized particles will be

$$I_i = e\beta_i K_i N_i = e\beta_i \gamma_i AN = 1.59 Q_{i\max} V \exp\left[-\frac{RT^2}{\omega q} V\right],$$

$$I_M = e\beta_M K_M N_M = e\beta_i \gamma_i AN = 1.59 Q_{M\max} V \exp\left[-\frac{RT^2}{\omega q} V\right],$$

$$I_S = I_M + \sum_z I_i = 1.59 Q_{\max} V \exp\left[-\frac{RT^2}{\omega q} V\right], \tag{4}$$

where I_i and I_M are the current of ions of neighboring types desorbed from the emitter, I_S – the total ion current recorded by the detector, $Q_{i\max}$ and $Q_{M\max}$ — charge of ions of neighboring types desorbed to the temperature of the maximum of spectra $T_{\max}$, $Q_{\max} = Q_{M\max} + \sum\limits_z Q_{i\max}$ — area charge of the TD spectrum up to $T_{\max}$, β_i and β_M — SI coefficients of particles of the corresponding types.

In the low-speed mode of the SI detector the solution of equations (2) and (3) for the regions $T_0 < T$, $N_0 < N$ and $V \le A$ (T_0 — initial temperature of the evaporator, N_0 — number of substance molecules adsorbed on the emitter surface at T_0) will be

$$N = \eta(n_0 - n) + N_0 - \int_{T_0}^{T} \frac{A}{\omega} N dT \approx \frac{\eta n V}{A - V + \omega q/RT^2},$$

$$I_i = K_i(Q_{i0} - Q_i) - eK_i E_i n \frac{A + \omega q/RT^2}{A - V + \omega q/RT^2},$$

$$I_M = K_M(Q_{M0} - Q_M) - eK_M E_M n \frac{A + \omega q/RT^2}{A - V + \omega q/RT^2},$$

$$I_S = K_M(Q_M^0 - Q_M) + \sum_z K_i(Q_i^0 - Q_i) - en \frac{A + \omega q/RT^2}{A - V + \omega q/RT^2}\left(E_M K_M + \sum_z E_i K_i\right), \tag{5}$$

where

$$Q_i = e\beta_i \int_{T_0}^{T} \frac{K_i N_i}{\omega} dT \quad \text{and} \quad Q_M = e\beta_M \int_{T_0}^{T} \frac{K_M N_M}{\omega} dT$$

— charge of molecular ions and ions of products of heterogeneous chemical reactions, desorbed to temperature T

of the evaporator; $Q_{0i} = eE_i n_0$ and $Q_{0M} = eE_M n_0$ — total charge of ions of the corresponding types desorbed over the entire period of the evaporator temperature sweep, sum of which is equal to the total charge of area of the TD spectrum of the analyte $Q_0 = Q_{M0} + \sum_i Q_{i0}$; $E_i = \eta\gamma_i\beta_i$ and $E_M = \eta\gamma_M\beta_M$ — ionization efficiencies of molecules to certain types of particles, the sum of which is equal to the ionization efficiency of substances $E = E_M + \sum_z E_i = \frac{Q_0}{en_0}$.

Relationships (1)–(5) are the theoretical basis of the method, which explains the regularity of the dependence of the spectra shape on the emitter temperature, kinetic parameters of heterogeneous processes and the rate of change of the flow of molecules of the analytes directed to the detector, and also the operation mode of the SI detector is selected also.

Studies of the spectrometer operation in the high- and low-speed modes of SI detector showed that both modes are suitable for tasks of physicochemical analysis. However, in the low-speed mode of the SI detector the spectrometer resolution with respect to temperatures of the maximum $T_{\max}$ deteriorates greatly, while in the high-speed mode the resolution is better, and the dependence of the ion current $I_s(t)$, in contrast to case of low speed, will repeat the dependencies of TD spectrometry. Therefore, the high-speed mode was selected. To determine this operation mode the method proposed by us in the paper [36] was used.

3. Results and discussion

Fig. 2 shows the basic TD spectra (a) and the linear range of SI (b) of chromatographically pure morphine recorded in the database of „Druggy“program of TD spectrometer. The maximum temperature $T_{\max}$ of morphine spectra ranges from 185 to 205°C and depends on the mass of morphine applied to the evaporator surface. In the studied region the mass of morphine $T_{\max}$ characterizes the temperature of the maximum of substances sublimation. $T_{\max}$ at masses below 10 ng characterizes the temperature of maximum of morphine molecules desorption from the evaporator surface. The linear range and ionization efficiency E are preserved. The ionization efficiency is $E = Q_0/en_0 = (4.4 \pm 0.4) \cdot 10^{-4}$.

Fig. 3 shows the TD spectra of extracted urine sample of heroin user and chromatographically pure morphine (50 ng). It can be seen that the spectrum of the biosample is wider than the spectrum of chromatographically pure morphine. Perhaps this is due to the presence of heroin metabolites in the obtained extracts and their ionization, since heroin is metabolized after contact, and approximately 80% of heroin is excreted in the urine within 24 h in the form of a metabolite of morphine-3-glucuronide, 6-monoacetylmorphine and morphine [37]. Despite this, the main component (morphine) appears clearly at $T_{\max} = 200$°C and coincides with the temperature of maximum of chromatographically pure

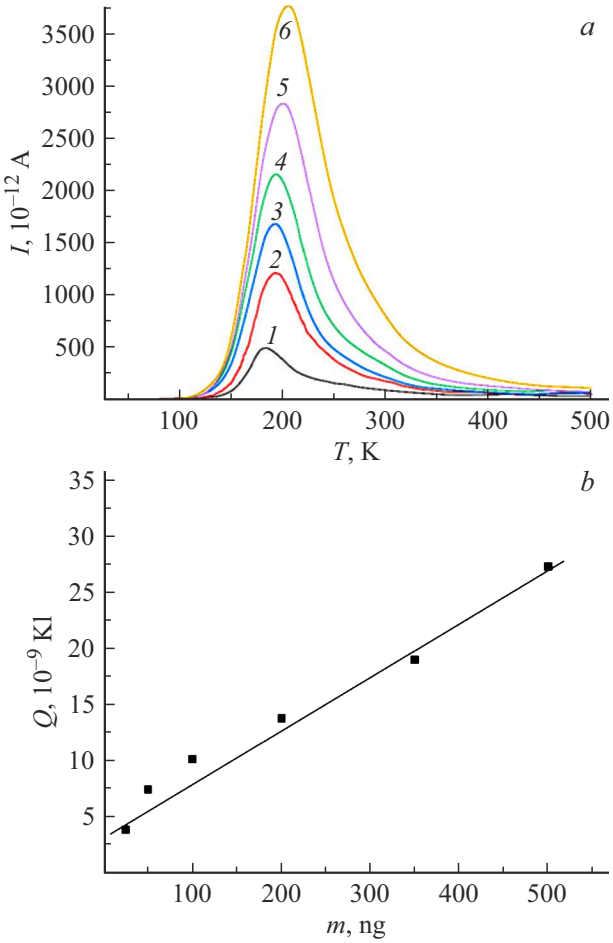

Figure 2. TD spectra (a) and the linear range of SI (b) of chromatographically pure morphine recorded in the database of „Druggy“ program of TD spectrometer. Masses of analyzed substances: *1* — 25, *2* — 50, *3* — 100, *4* — 200, *5* — 350, *6* — 500 ng.

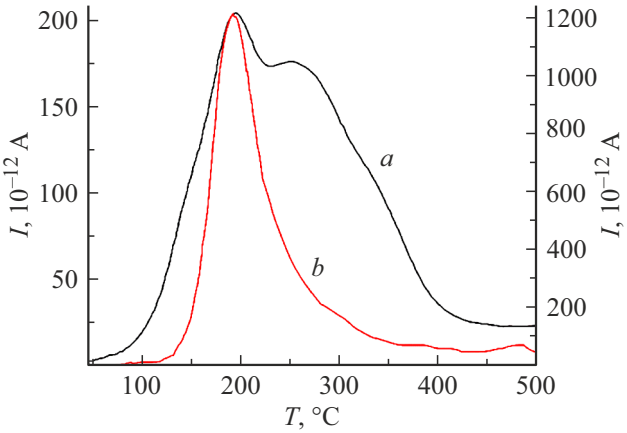

Figure 3. TD SI spectra of urine extracts of heroin user (a) and chromatographically pure morphine (b).

morphine, which makes it possible to estimate the amount of morphine in the studied sample. To determine the

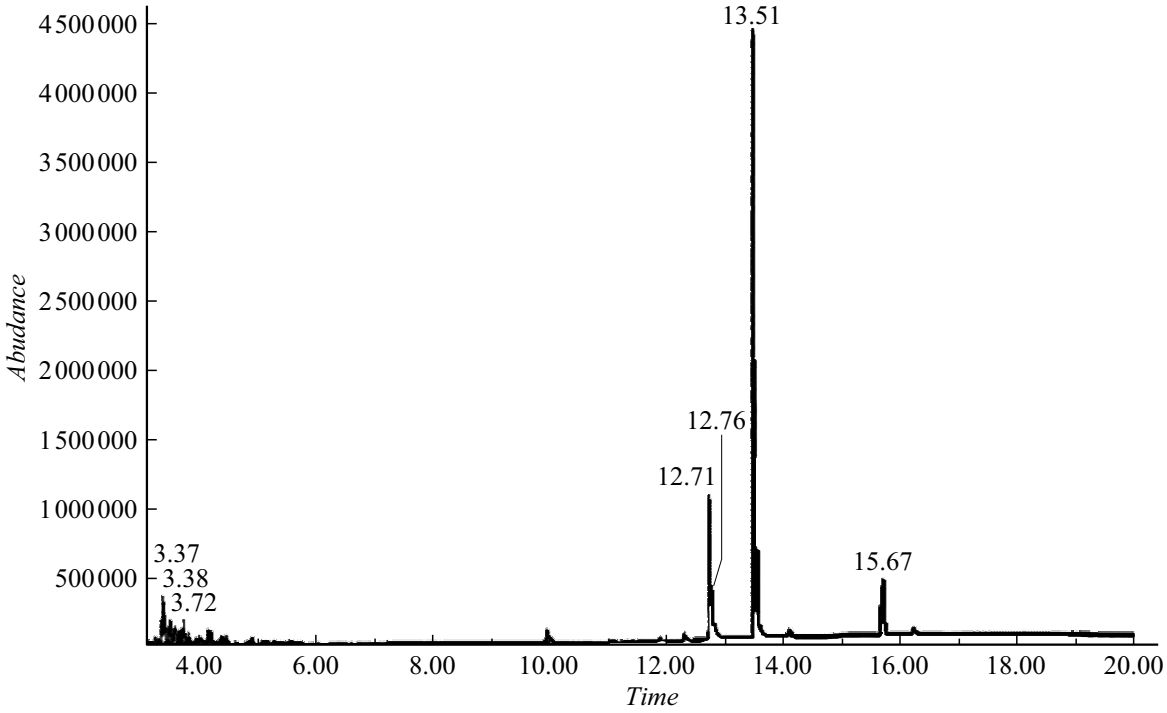

Figure 4. Chromatogram of cannabis extract in ethyl alcohol.

mass m_0 of morphine in the test sample it is necessary to calculate the charge area of the spectrum of the test sample covered by the TD spectrum of chromatographically pure morphine. After such area of the spectrum calculation we obtained the values $Q_0 = 1.3 \cdot 10^{-9}$C, this corresponds to ~ 9 ng mass of morphine in the analyzed sample.

Cannabis (Cannabis sativa, Cannabinaceae) contains about 30 derivatives of 2-(2-isopropyl-5-methylphenyl)-5-pentylresorsinol, known as cannabinoids. The most important among them are tetrahydrocannabinols with psychomimetic activity, as well as cannabidiol (CBD), cannabinol (CBN) and Δ^9-tetrahydrocannabinoleic acid, which are converted into active form during plant growth and consumption (when smoking).

Depending on climatic conditions, genetic factor, storage and processing conditions the content of THC in cannabis ranges from 0.1 to 5%. Fig. 4 shows the chromatogram of the № 1320 sample experimentally studied by GC/MS. It can be seen from the chromatogram that the cannabis extract consists mainly of Δ^9-THC (Rt = 13.51 min), CBD (Rt = 12.71 min) and CBN (Rt = 15.67 min), which can serve as indicator components in the study of cannabis extracts, as well as their traces in blood and urine extracts of cannabis users using TD spectrometry.

Fig. 5 shows basic TD spectra of chromatographically pure Δ^9-THC (*a*), CBD (*b*) and CBN (*v*). They have rather narrow TD spectra characteristic of each substance, and the temperature of maximum $T_{\max}$, which shifts to high temperatures with an increase in the amount of substance applied to the evaporator. As can be seen from the spectra, $T_{\max}$ for CBN is 125–142°C, for CBD — 125–139°C, and for Δ^9-THC — 143–152°C. The ionization efficiencies are $E = (1.6 \pm 0.16) \cdot 10^{-4}$, $E = (0.72 \pm 0.7) \cdot 10^{-5}$ and $E = (9.4 \pm 0.9) \cdot 10^{-5}$ respectively.

Taking into account the high efficiency of ionization of the main components of cannabis extracts (Fig. 4), using the TD spectra of artificial mixtures of Δ^9-THC, CBD and CBN one can identify trace amounts of cannabinoids in complex solutions, including extracts of biosamples of users of these substances. Fig. 6 shows the TD spectra of artificial mixture of chromatographically pure cannabinoids Δ^9-THC, CBD and CBN (*a*), cannabis extract (*b*), as well as extract of blood (*c*) and urine (*d*) of cannabis user. From the TD spectra of the cannabis extract, as well as the extract of urine and blood of the cannabis user, it can be seen that they appear as broad lines with a characteristic temperature maximum corresponding to the superposition of cannabinoids. Despite this, the TD spectra of the extracts have a pronounced temperature of maximum $T_{\max}$ characteristic for mixture of cannabinoids, which indicates the presence of traces of cannabinoids in biosamples. Also from Fig. 6b it can be seen that $T_{\max}$ of TD spectrum for the cannabis extract is higher (by ~ 6°C) than for the other samples. This is due to the higher concentration of Δ^9-THC relative to CBN and CBD (Fig. 4), since $T_{\max}$ Δ^9-THC is higher than for CBN and CBD.

Conclusion

Thus, the developed relatively simple method and TD spectrometer made it possible to identify and carry out a

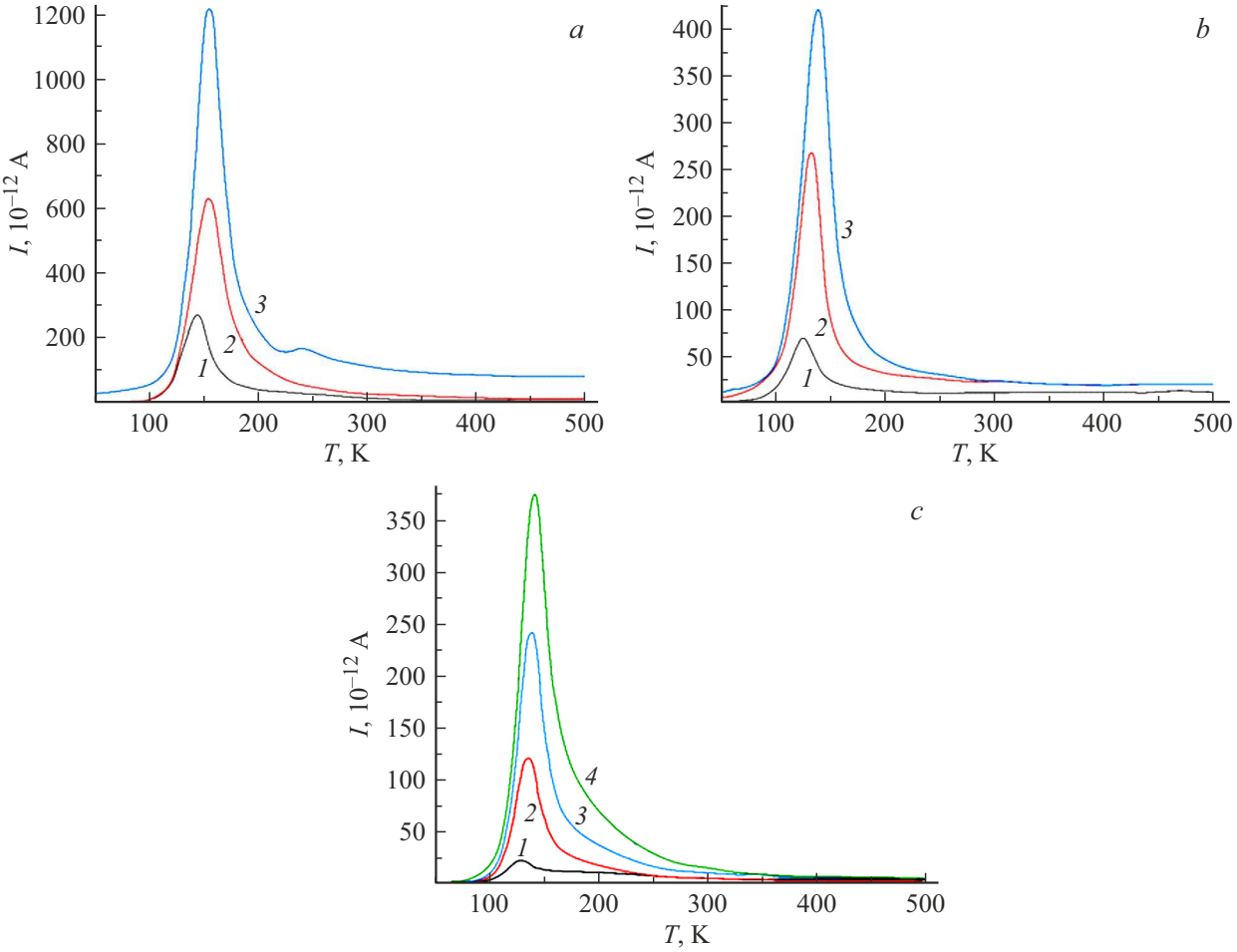

Figure 5. TD spectra of chromatographically pure Δ^9-THC (*a*), CBD (*b*) and CBN (*c*). Masses of analyzed substances: *a* — 100 (*1*), 200 (*2*), 300 ng (*3*); *b* — 50 (*1*), 100 (*2*), 200 ng (*3*); *c* — 10 (*1*), 50 (*2*), 100 (*3*), 200 ng (*4*).

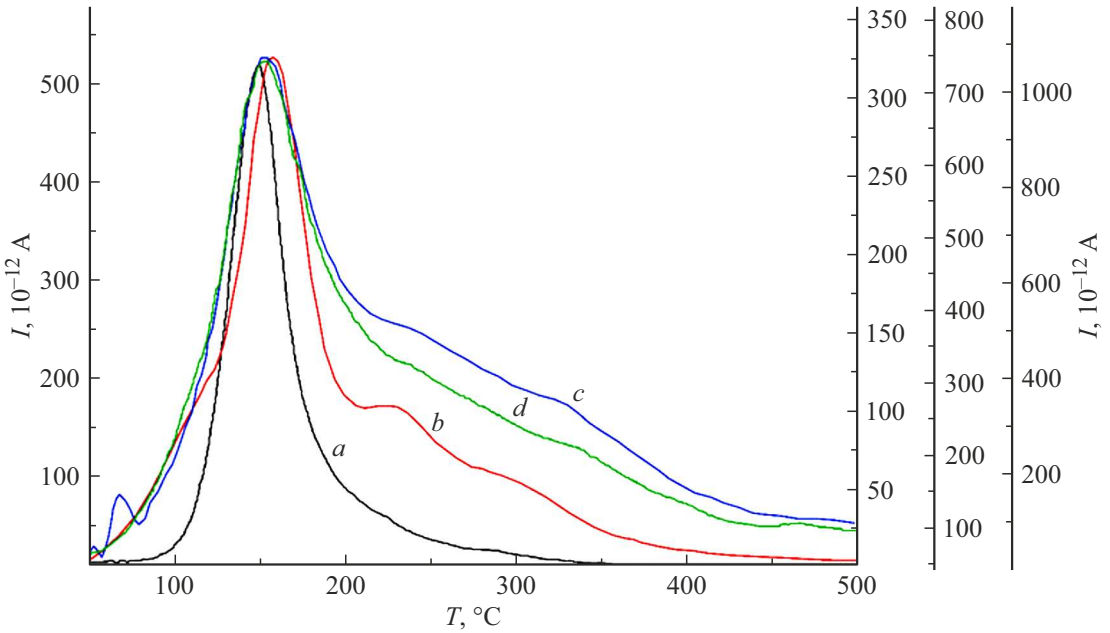

Figure 6. TD spectra: *a* — artificial mixture of chromatographically pure cannabinoids Δ^9-THC (100 ng), CBD (50 ng) and CBN (50 ng); *b* — cannabis extract; *c* — blood extract; *d* — urine extract of cannabis user.

quantitative analysis of traces of heroin (morphine, which is a metabolite of heroin) and cannabinoids in extracted samples without chromatographic and mass spectrometric separations.

Further studies of the regularities of SI of AOC and their metabalites in various biosamples, as well as the development of the analysis method and the technology of the TD spectrometer can bring closer the solution of a number of problems in analytical chemistry by express direct (selective) analysis of biosamples.

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Conflict of interest

The authors declare that they have no conflict of interest.

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