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Express analysis of explosives, chemical warfare agents and drugs with multicapillary column gas chromatography and ion mobility increment spectrometry

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Abstract

Description of a gas chromatograph designed for express analysis of explosives (2,4-dinitrotoluene, 2,4,6-trinitrotoluene, pentaerythritol tetranitrate), chemical warfare agents (mustard gas, lewisite, sarin) and drugs (heroin, cocaine hydrochloride, crack) is given. The devices comprises a multicapillary chromatographic column and an ion mobility increment spectrometer (MCC–IMIS). The main analytical characteristics of an IMIS (estimated detection limit (DL), linear dynamic range (LDR), speed of response) and a chromatographic column (separation power, degree of separation, a number of possible peaks at a chromatogram section, divided by analysis time) are determined. The maximum value of DL equal to 5 pg/ml was registered for *cis*-α-LW, and the lowest one of 0.001 pg/ml was for cocaine. The maximum value of LDR equal to 1000 was registered for sarin and the lowest one of 150 was for the ions of lewisite. Speed of response of one compound detection with the IMIS was 0.7 s.

Keywords: Ion mobility increment spectrometry; Explosives; Chemical warfare agents; Heroin; Cocaine; Crack

1. Introduction

The essential features required of devices used under field conditions to detect vapors of explosives, chemical warfare agents and drugs (EAD) in air are:

- law detection limit;
- high selectivity (specificity);
- law response time;
- capacity of compound identification;
- portability.

Ion mobility spectrometers (IMS) and gas chromatographs with IMS as a detector [1–3], as well as a gas chromatograph that uses a multicapillary column and an ion mobility increment spectrometer as a detector [4] meet these requirements.

A multicapillary gas chromatographic column (MCC) is a glass bundle of 1000 longitudinal parallel uniform capillaries 20/100 μm in diameter coated with a stationary liquid phase (SLP). The MCC is characterized by a high separation rate (100 theoretical plates (t.p.)/s) and an efficiency of about 15 000 t.p./m [5]. Fig. 1 shows microphotos of the MCC's cross-section and a fragment of it.

An ion mobility increment spectrometer (IMIS) belongs to the devices of an ionization type. Like an ion mobility spectrometer (IMS), the operation of IMIS rests on sampling air containing a mixture of trace constituents, its ionization, spatial separation of produced ions in gas (e.g., purified air) and separated ions detection. IMIS differs from IMS in that ions of different types are separated in IMIS by ion mobility increment that depends on electric field strength [6]. The commonly accepted name for this type of the device is not available. The names like field ion spectrometer [7], high-field asymmetric waveform ion mobility spectrometer [8] are used as a synonym for IMIS.

Ion drift velocity V caused by an action of electric field E is [9]:

$$V = K(E)E; \quad K\left(\frac{E}{N}\right) = K_0\left(1 + \alpha\left(\frac{E}{N}\right)\right) = K_0\left(1 + \sum_{n=1}^{\infty}\alpha_{2n}\left(\frac{E}{N}\right)^{2n}\right), \tag{1}$$

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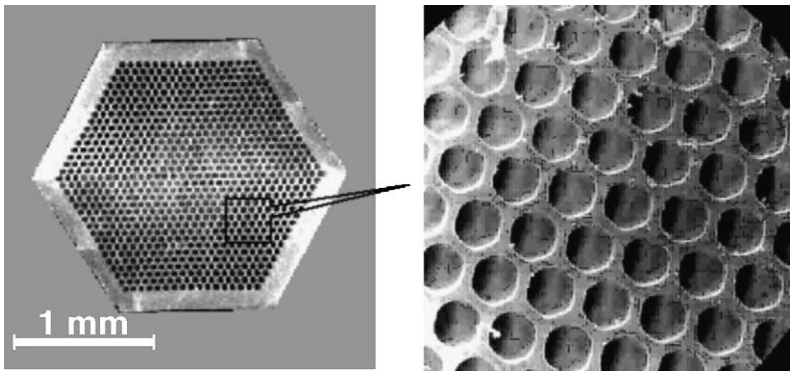

Fig. 1. Microphotos of the MCC's cross-section and a fragment of it.

where K_0 ($cm^2\ V^{-1}\ c^{-1}$) is the mobility coefficient in a weak field, N is neutral gas density, $\alpha(E/N)$ is the mobility coefficient increment, α_{2n} are decomposition coefficients, $n \geq 1$ is an integer. Under the action of periodic alternating asymmetric waveform field, $E_d(t)$ ions executing fast oscillatory motions with period T drift with average velocity $\langle V_i \rangle$ characteristic for each ith component proportional to $\alpha_i(E/N)$. The field $E_d(t)$ should meet the requirements [10]:

$$E_d(t) = E_d f(t)$$
$$\int_t^{t+T} f(t)\,dt = 0,\ \frac{1}{T}\int_t^{t+T} f^{2n+1}(t)\,dt \equiv \langle f^{2n+1} \rangle \neq 0, \tag{2}$$

where E_d is an amplitude, $f(t)$ is a form of the field, T is period. Should the ion drift of the ith component be compensated by constant electric field E_{ci}, the ion velocity will be zero:

$$\langle V_i \rangle = \langle K_0(1+\alpha_i)(E_d f(t) - E_{ci} \rangle = 0. \tag{3}$$

The compensation field of the ith component is expressed by substituting decomposition of coefficient α from (1) into Eq. (3) and using condition (2) and approximation $(E_d - E_c)^n \approx E_d^n - nE_d^{n-1}E_c$, with $|E_d| \gg |E_c|$ [6]:

$$E_{ci} \approx \frac{E_d \sum_{n=1}^{\infty} \alpha_{i2n}(E_d/N)^{2n} \langle f^{2n+1} \rangle}{1 + \sum_{n=1}^{\infty}(2n+1)\alpha_{i2n}(E_d/N)^{2n}\langle f^{2n} \rangle}. \tag{4}$$

The ions for which $\langle V_i \rangle = 0$ are transported to a collector with a carrier-gas, the other ions leave a separation area and recombine. With E_c changing, spectrum of a mixture of ions of all types is recorded.

The separation rate of the MCC combined with the identification reliability of the IMIS provide the basis for a promising usage of this tandem for express analysis of samples containing EAD.

The aim of this paper was to determine the main characteristics of a gas chromatograph (GC) provided with a multicapillary column and an ion mobility increment spectrometer as a detector upon express analysis of explosives (2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN)), CW-agents (sarin (GB), mustard gas (HD), isomers of α-lewisite (α-LW)) and drugs (heroin, cocaine hydrochloride, crack).

2. Experimental

2.1. Instrumentation

The GC-IMIS was developed in DTIIEGE (Novosibirsk, Russia). A block diagram of GC-IMIS is given on Fig. 2, GC consists of a syringe injector-evaporator and MCC placed in a thermostat heater. The MCC (DTIIEGE, Novosibirsk, Russia) has a length of 0.22 m, a volume of 0.45 ml and capillaries 40 μm in diameter. SE-30, OV-624 (Chromresurs, Moscow, Russia) ~0.2 μm thick were used as a SLP. As a mobile phase, dry air was used (water vapor concentration $C_{H_2O} \leq 1 \times 10^{16}\ cm^{-3}$). For dehumidification, a filter containing 1.4 l of silica gel (∅ 0.3 cm) and 0.3 l of 13X zeolite (Reachem, Moscow, Russia) was used. Analysis was

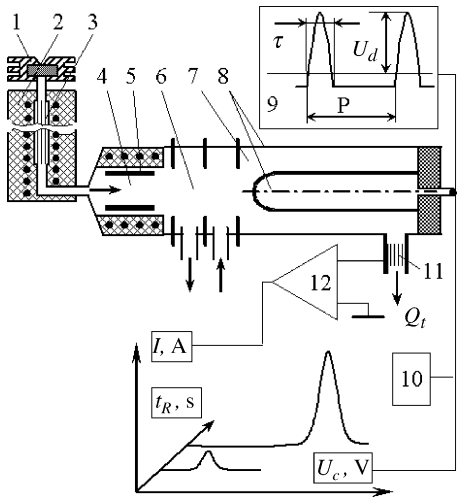

Fig. 2. The block diagram of GC-IMIS. 1: syringe injector-evaporator; 2: thermostat; 3: MCC; 4: ionization chamber; 5: β-source ^{63}Ni; 6: gas seal; 7: ion separation chamber; 8: electrodes; 9: dispersion voltage generator; 10: compensation voltage generator; 11: ion collector; 12: electrometer.

performed under isothermal conditions with temperature of syringe injector-evaporator, T_v of 190 °C and column temperature, T_c = 60, 75, 150, and 175 °C.

The IMIS comprises an ionization chamber, a gas seal, an ion separation chamber, an ion detector and voltage generators. The ionization chamber is a heated cylindrical cavity 1 cm in diameter and in length provided with ^{63}Ni β-source (Izotop, St. Petersburg, Russia) with an activity of 10 mCi. To transport ions from the ionization chamber into the separation one, we used electric field created in the gas seal, in which ions from the ionization chamber moved towards the dry purified air flow that prevented non-ionized background noise (water vapor, volatile components of SLP) from entering the separation chamber. The background noise is capable to change the properties of a gaseous medium and to affect the process of analyzed ions separation.

An ion separation chamber kept at room temperature is formed by two electrodes which are coaxial cylinders, $r_1 = 1$ and $r_2 = 0.68$ cm in diameter and 7 cm in length, the chamber is purged with a carrier gas (dry air). The electrodes are connected to compensation voltage and asymmetric waveform voltage generators. The generator has the following parameters: voltage form (Fig. 2)

$$f(t) = \frac{\sin[\pi(t - mT)/\tau] - (2\tau/\pi T)}{1 - 2\tau/\pi T}, \quad \text{with } mT \le t \le (mT + \tau);$$
$$f(t) = -\frac{2\tau/\pi T}{1 - 2\tau/\pi T}, \quad \text{with } (mT + \tau) \le t \le (m + 1)T, \tag{5}$$

($m \ge 0$ is an integer); high-voltage pulse duration, τ = 2 μs, period, T = 6 μs, dispersion voltage amplitude, U_d = 1/4 kV. We used an oscillograph S1-114 (l/b V-2150, Minsk, Byelorussia) to control the form and amplitude of the $U_d(t)$ voltage. Ions of different types were separated by an ion mobility increment dependent on electric field strength. An ion detector includes a collector and an electrometer. Absolute error in compensation voltage measurement is $\delta U_c = \pm 0.05$ V; relative measuring error of the compensation voltage is $\delta U_c = \pm 1\%$, asymmetric waveform voltage amplitude is $\delta U_d = \pm 7\%$ and time interval is $\delta t = \pm 7\%$.

2.2. Chemicals

For experiments we used: acetone solutions of DNT: 3×10^{-3} g/l; TNT: 2.5×10^{-4} g/l; PETN: 1.4×10^{-4} g/l; commercial TNT: 4×10^{-4} g/l; methanol solution of: GB: 1×10^{-3} g/l; HD: 1×10^{-3} g/l; isopropanol solutions of α-LW: 1×10^{-2} g/l; ethanol solutions of heroin: 0.88 g/l; cocaine hydrochloride: 1 g/l; crack: 1 g/l.

The solutions were obtained from the Research Institute of Special Technics and Communication (Novosibirsk, Russia).

Samples were injected with a syringe of volume 1 μl (Hamilton Company, Reno, Nevada).

3. Results and discussion

3.1. Selective detection of EAD with GC-IMIS

The IMIS spectrum is the compensation voltage dependence of the ion current, $I(U_c)$, therewith each ion type is recorded as an ion peak. Value, U_c, corresponding to a peak maximum is registered when relation (4) is hold and is dependent on individual ion parameters (mass, structure, interaction potential), dispersion voltage amplitude, U_d, atmospheric pressure and drift gas composition, and can be used for identification. Table 1 shows the main types of ion-molecule reactions into which the molecules of tested compounds enter being ionized by β-source at atmospheric pressure, mass-charge ratio (m/z) and types of ions produced. In the last column, one can find references to the papers where these ions were identified by mass-spectrometry.

Fig. 3 gives drift spectra in negative and positive modes obtained with the best value of U_d^{opt} (Table 2), when an air sample containing vapors of: (a) a mixture of DNT, TNT and PETN, (b) HD, (c) a mixture of *cis*- and *trans*-α-LW isomers, (d) GB, (e) cocaine is fed directly to the input of the IMIS. It is evident from Fig. 3 that the ion peaks of each compound have compensation voltage values, U_c, typical of a particular compound. The cocaine peak is partially overlapped by the peak of positive reactant ions (RI) (Fig. 3e), while the HD peak is well separated from the negative RI (Fig. 3b). On the other spectra, RI lie inside the spectra, since the U_d^{opt} are high. Standard deviation that defines the repeatability of

Table 1
The main types of ion-molecule reactions, mass-charge ratio (m/z) and types of ions produced (M is molecule of a compound, H is hydrogen atom, R is a molecule fragment).

Compound	Reaction	m/z	Ion	References
DNT	Proton abstraction	181	$(M–H)^-$	[11,12]
TNT		226		
PETN	Electrophilic capture	316, 378	M^-, $M*NO_3^-$	[13]
GB	Associative proton capture	141	$(M+H)^+$	[14]
HD	Dissociative electron transfer	35	Cl^-	[15]
α-LW	Electrophilic capture	241–249	$M*Cl^-$, $(M–R)*Cl^-$	[16]
Cocaine	Proton transfer	182	MH^+	[17]
Heroin	Electron abstraction	369, 310	M^+, $(M–CH_3CO_2)^+$	[18]

Table 2
The main analytical characteristics of the IMIS on detecting vapors EAD

Compound	Sign	U_d^{opt} (kV)	U_c (V)	DL (pg/ml)	LDR	w_U(V)	R
DNT	–	−3.4	12.9	0.016	260	1.2	10.8
TNT	–	−3.4	9	0.014	300	0.7	10.4
PETN	–	−2.6	2.1	0.008	5	1.1	1.9
HD	–	−1.6	12.4	1	200	1.5	8.3
Cis-α-LW	–	−1.9	4.7	5	150	0.38	12.4
Trans-α-LW	–	−1.9	6.2	3		0.45	13.8
GB	+	2.2	–5.1	0.2	1000	0.5	10.2
Cocaine	+	−4	–3.1	0.001	600	1.7	1.9
Crack	+	−4	–3.1	–	–	1.7	1.9
Heroin	+	5.2	3.8	–	–	2.3	1.7

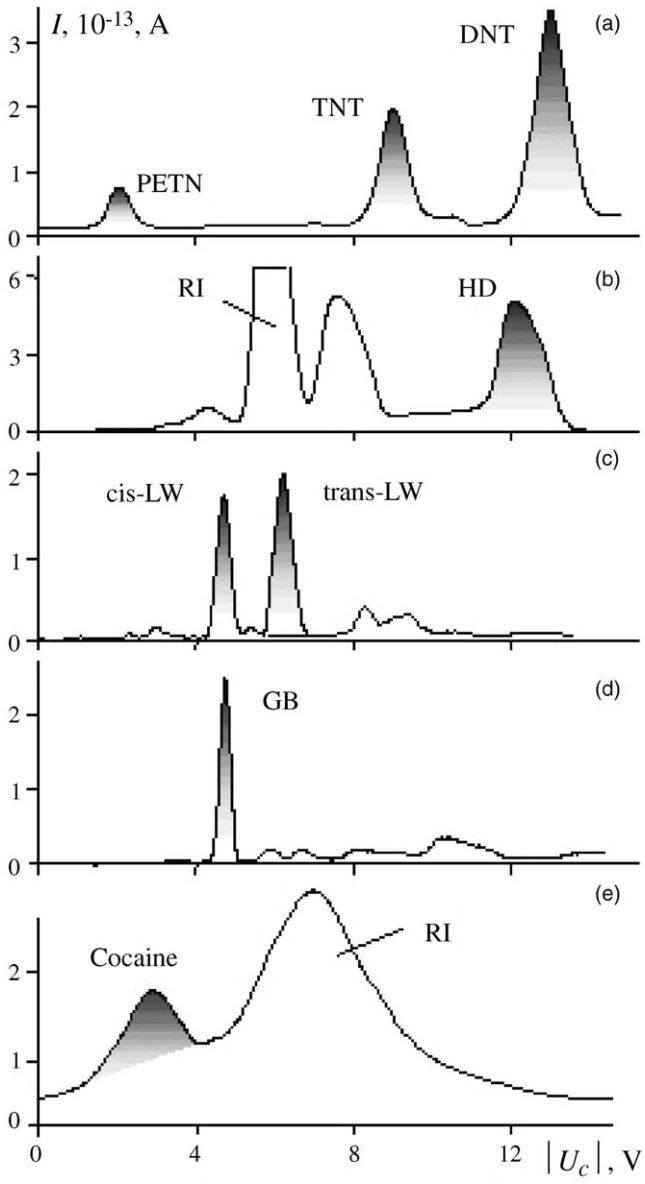

Fig. 3. Drift spectra of air containing vapours of: (a) a mixture of DNT, TNT and PETN, (b) HD, (c) a mixture of *cis*- and *trans*-α-LW isomers, (d) GB, (e) cocaine.

voltage, U_c, on recording individual compound spectra was $\sigma_{Uc1} = \pm 1\%$ within 1 day and $\sigma_{Uc5} = \pm 2\%$ within 5 days (the number of measurements of each compound was $b =$ 15 per day). When U_c was adjusted to the standard pressure (760 mm Hg), standard deviations were $\sigma_{Uc1} \approx \sigma_{Uc5}$.

There are two ways to record chromatograms with the GC-IMIS in gas chromatographic studies: (1) with constant U_c, (2) on recording spectra. With U_c set to detect a given compound, the peak of the compound alone is found on the chromatogram of a compound mixture provided that the IMIS separates the peaks of tested compounds from each other. Fig. 4 shows typical chromatograms of: (a) DNT, TNT, PETN (when a mixture of these compounds is analyzed, and U_d^{opt} is set for a definite compound whose chromatogram is recorded), (b) *cis*- and *trans*-α-LW isomers, GB, HD, (c) heroin and cocaine. It is evident that in keeping with the chosen U_c value each chromatogram contains a peak of one compound. Standard deviation, that defines the repeatability of retention time, t_R, on recording individual compound chromatogram was $\sigma_{t_R} < \pm 0.5\%$ within five days (the number of measurements of each compound was $b = 10$ per day).

When the IMIS operates in a spectra record mode, chromatographic results are displayed as a chromato-drift-spectrum which presents a three-dimensional curve with compensation voltage, U_c, retention time, t_R, and ion current, I, plotted as X, Y and Z-axes, respectively. As an example, Fig. 5 shows a chromato-drift-spectrum of commercial TNT in acetone solution recorded as U_c changed in the range: 1.5/3.7 V ($U_d = -1.8$ κV). Spectra were recorded every second. Peaks of TNT ($U_c = 1.6$ V, retention time, $t_R = 17$ s) and attached foreign DNT ($U_c = 3.4$ V, $t_R = 9$ s) were present in spectra.

3.2. Analytical characteristics of the IMIS

Table 2 gives the main analytical characteristics of the IMIS: detection limit (DL), linear dynamic range (LDR), compensation voltage (U_c) registered with the value of dispersion voltage amplitude (U_d^{opt}) the best for a given compound, peak width at half height (w_U), resolution (R) and signs of analyzed compound peaks. When vapors of both

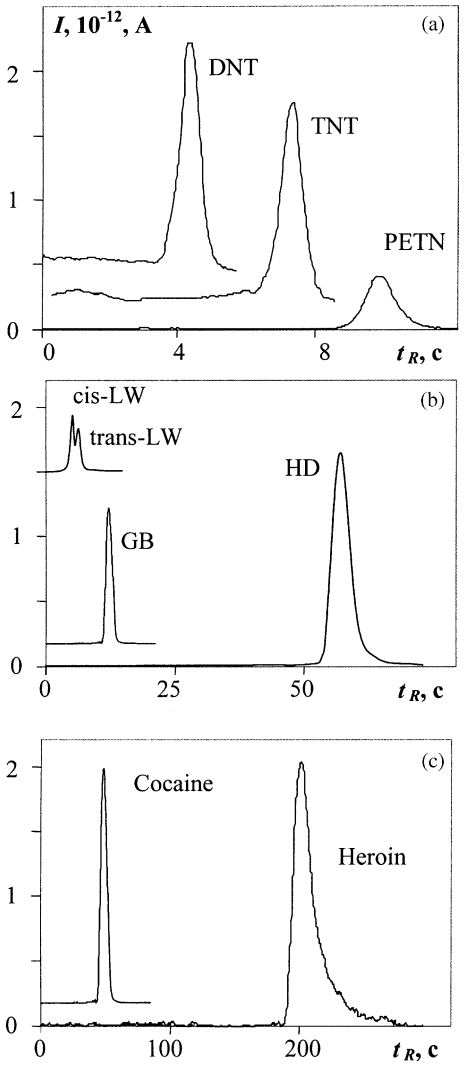

Fig. 4. Chromatograms of solutions: (a) a mixture of DNT, TNT and PETN with U_c equal to 12.9 V, 7.3, 2.1 V, respectively; (b) *cis*- and *trans*-α-LW isomers, GB, HD; (c) a mixture of heroin and cocaine with U_c equal to 3.8 V и −3.1 V, respectively. Conditions of chromatographic analysis: $t_{in} = 0.4$ s, $T_c = 175\,^{\circ}$C, $Q_c = 0.8$ ml/s.

crack and its solution are analyzed, the main detected fraction is cocaine. Thus, the main analytical characteristics of the IMIS (except detection limit) and the GC-IMIS on detecting cocaine and crack coincide and are combined within a single row in the Table. The values of U_d^{opt} were determined earlier in [19–21].

For negative ions of DNT, TNT, PETN, HD and LW a positive value of voltage, U_c, with U_d^{opt} being negative, testifies that $\alpha(E/N)$ is positive, and mobility coefficient, K, grows with the U_d voltage. For positive ions of GB, ($U_c > 0, U_d < 0$) $\alpha(E/N) > 0$, and K grows with voltage, U_d, whereas for cocaine ($U_c < 0, U_d < 0$) and heroin ($U_c > 0, U_d > 0$) α(E/N) is negative, their mobility coefficient decreases as voltage, U_d, increases.

Detection limit (DL) and linear dynamic range (LDR) were determined earlier [4,19–21] with a gas-vapor mixture

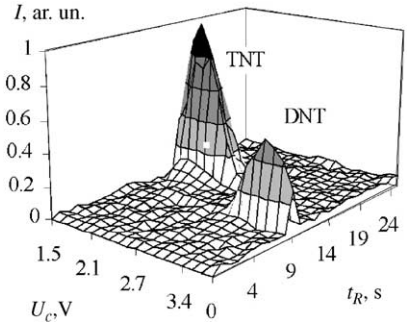

Fig. 5. A chromato-drift-spectrum of commercial TNT in acetone solution. Conditions of chromatographic analysis: $t_{in} = 0.4$ s, $T_c = 150\,^{\circ}$C, $Q_c = 0.5$ ml/s. Parameters of IMIS: $U_d = -1,8$ kV compensation voltage variation in the range: $U_c = 1.5 \div 3.7$ V.

fed directly to the IMIS input and the best values of voltage, U_d^{opt}. The maximum value of DL equal to 5 pg/ml was registered for *cis*-α-LW, and the lowest one of 0.001 pg/ml was for cocaine. Heroin vapors at room temperature were not detected due to a very low saturated vapor concentration (0.006 pg/ml) [22]. To obtain the parameters of the IMIS for heroin, the compound was heated. LDR for PETN and heroin was limited by the concentration range covered and made up 5 and 600, respectively.

Resolution is among the most important characteristics of a spectral device and accounts for its capacity to separates components of an analyzed mixture. The IMIS resolution can be expressed by the relationship among the main parameters of ion peak on a drift spectrum: compensation voltage and peak width at half height ($R = U_c/w_U$). From the experimental values of w_U and R given in Table 2 follows that *trans*-α-LW gave the highest resolution of 13.8, and PETN, cocaine and heroin gave the lowest one.

3.3. Analytical characteristics of the GC-IMIS

Table 3 gives the main analytical characteristics of the GC-IMIS: retention time in a column (t_R), chromatographic

Table 3
The main analytical characteristics of the GCIMIS on analyzing solutions EAD

Compound	A			B		
	t_R (s)	w_t (s)	N_c	t_R (s)	w_t (s)	N_c
DNT	9	1	449	4.5	0.7	229
TNT	17	1.3	947	7.8	0.9	416
PETN	26	1.6	1463	10.4	1	599
Cocaine, crack	226	14	1443	51	3	1601
Heroin				206	10.4	2174
Gb[a]	12.3	1.4	428			
HD[b]	55	3.2	1600			
cis-α-LW	4.9	0.8	200			
trans-α-LW	6	0.9	228			

[a] $T_c = 60\,^{\circ}$C.
[b] $T_c = 75\,^{\circ}$C.

peak width at half height (w_t), separation efficiency characterized by a number of theoretical plates, $N = 5.54(t_R/w_t)^2$, under different analysis conditions: (A) $T_c = 150\,^\circ$C (except GB ($T_c = 60\,^\circ$C) and HD ($T_c = 75\,^\circ$C) and $Q_c = 0.5$ ml/s, $t_M = 2.1$ s; (B) $T_c = 175\,^\circ$C; $Q_c = 0.8$ ml/s, $t_M = 1.5$ s (t_M is a retention time of a nonsorbing component). Heroin was not analyzed at $T_c = 150\,^\circ$C due to a high retention time (more than 10 min).

One can see from the Table that an increase in T_c and Q_c results in considerable decrease of t_R and cuts down the separation time of a mixture of explosives from 30 to 12 s and cocaine from 240 to 55 s. As for the explosives with a low retention time, separation efficiency reduces by a factor of 2/2.5 as T_c and Q_c increase. Dead volume and diffusion processes present in the sample injector, connecting lines and the IMIS itself are responsible for this. Sample injection time, $t_{in} = 0.4c$, makes a modest contribution to the peak widening with the low t_R values. The value of t_{in} was chosen so as to reduce peak diffusion and to achieve complete sample injection. With $t_{in} = 0.4c$ 80% of a sample is injected and diffusion (decrease in a chromatographic peak amplitude) does not exceed 10 times with a separation time of 1 min.

On analyzing lewisite solution, two peak with retention time (t_R) were observed on the chromatogram: of *cis*-α-lewisite with $t_R = 4.9$ s and of *trans*-α-lewisite with $t_R = 6$ s. The peaks took their names based on t_R and data on the lewisite composition and boiling temperatures taken from literature [23]. T_c increased to 175 °C causes a sharp decrease in the amplitude of lewisite peaks, which is likely to be due to the increased thermal decomposition process and transformation of α-lewisite into β-and γ-lewisite.

A minimum amount of a compound detected with the GC-IMIS was determined for the solutions of TNT and PETN alone with $T_c = 175\,^\circ$C and $Q_c = 0.8$ ml/s and made up 2 and 4 pg, respectively. It is appropriate at this point to evaluate the detection limit of the GC-IMIS on analyzing vapor phase with the use of a concentrator injector. From the experimental data obtained in [24] the detection limit of the GC-IMIS for TNT with a grid concentrator is expected to be no more than 0.0014 pg/cm^3.

When express analysis is performed, one should consider the chromatographic column characteristics divided by analysis time. Separation power, N_t, degree of separation, R_t, and number of possible peaks, Z_t, at a length of a chromatogram for tested compound are given in Table 4 with different T_c and Q_c.

The separation power of a chromatographic peak was determined as the ratio between the separation efficiency and retention time of a given compound [25]:

$$N_t = \frac{N}{t_R}. \tag{6}$$

As one can see from Table 4, a decrease in t_R for the explosives does not cause considerable variations in separation power, whereas for cocaine the value of N_t varies inversely with t_R.

Degree of separation, R_t, divided by time was determined from expression [25]:

$$R_t = \frac{R_c}{\sqrt{t_{R2}}} = 1.177\frac{(t_{R2} - t_{R1})}{(w_{t2} + w_{t1})\sqrt{t_{R2}}}, \tag{7}$$

R_c is a degree of two compounds separation on a chromatogram, t_{R1}, t_{R2}, w_{t1}, w_{t2} are the retention time and half width of the first and second compounds, respectively, with $t_{R1} < t_{R2}$. The values of R_t for the pairs of DNT–TNT, TNT–PETN and cocaine–heroin are given in Table 4. An increase of T_c and Q_c for the explosives tends to decrease R_t.

Segments of the DNT–PETN and cocaine–heroin chromatogram were used to determine parameter, Z_t. For calculations we used expression [25]:

$$Z_t = \frac{Z_c}{\sqrt{t_{R2}}} = \omega \ln\left[\frac{t_{R2} - t_M + \omega w_M}{t_{R1} - t_M + \omega w_M}\right], \tag{8}$$

where Z_c is a number of possible peaks at a length of a chromatogram, ω is a separation factor as a measure of successive peak widening, w_M is a width of a possible zero peak base, $t_{R1} < t_{R2}$. Parameters, ω and w_M, were calculated by the experimental data for t_R, w_t and t_M with a least-squares

Table 4
The chromatographic column characteristics divided by analysis time

Compound	A				B			
	N_t (s^{-1})	R_t ($s^{-1/2}$)		Z_t ($s^{-1/2}$)	N_t (s^{-1})	R_t ($s^{-1/2}$)		Z_t ($s^{-1/2}$)
DNT	50	0.99	–	1.53	51	0.87	–	1.27
TNT	56		0.72		53		0.55	
PETN	56	–			58	–		
Cocaine	6.4				31	0.95	–	1.07
Crack								
Heroin					10.6		–	
cis-α-LW	41	0.28	1.4					
trans-α-LW	38							
GB	34							
MG	29							

technique using the expression:

$$1.7w_{ti} = w_M + \frac{t_{Ri} - t_M}{\omega}. \quad (9)$$

Numerical values of ω and $w_M$with different separation conditions were for explosives: (A) $\omega = 16.7$, $w_M = 1.3$ s, $Z_c = 7.8$; (B) $\omega = 11.5$, $w_M = 0.94$ s, $Z_c = 4.1$; for drugs: $\omega = 12.3$, $w_M = 1.08$ s, $Z_c = 15.3$. As evident from the Table, an increase in T_c and Q_c, tends to decrease Z_t.

A comparison of the N_t, R_t and Z_t values, the separation conditions being different, allows one to conclude that $T_c = 150\,^{\circ}$C and $Q_c = 0.5$ ml/s are preferred by express analysis of explosives, whereas the conditions where $T_c = 175\,^{\circ}$C and $Q_c = 0.8$ ml/s are more advantageous for cocaine and heroin. Temperature, T_c, equal to 175 °C is the maximum one, since the column that is used at a temperature higher than the above-mentioned for a long time tends to degrade, and the action of oxygen affect its analytical parameters.

3.4. Degree of separation in the GC-IMIS tandem

The availability of two components (the column and IMIS) in the device enhances a degree of separation, since the chromatographic compound separation in the column is supplemented with the ion separation by the ion mobility coefficient in the IMIS.

In chromatography, a degree of two compounds separation is determined by the R_c value. A condition of an adequate separation of two peaks is the equality: $R_c = 1$. For a complete separation $R_c \geq 1.5$, with $R_c \leq 0.5$ separation is unavailable.

When it is supposed that the shape of the peaks registered with the IMIS follows the Gaussian distribution, by analogy with a chromatography a degree of separation of two drift-spectrum peaks can be determined from the expression:

$$R_d = 1.177\frac{U_{c2} - U_{c1}}{w_{u2} + w_{u1}}, \quad (10)$$

where U_{c1}, U_{c2}, w_{u1}, w_{u2} are the compensation voltage and width at half height of the first and second peaks, respectively.

Since the processes of the chromatographic separation and separation by the ion mobility coefficient are independent, an expression for a degree of two compounds separation with the GC-IMIS tandem can be represented as:

$$R_{cd} = \sqrt{R_c^2 + R_d^2}. \quad (11)$$

In this case, a sufficient separation of two peaks with the GC-IMIS tandem ($R_{cd} = 1$) is achieved with the values of $R_c = R_d = 0.7$, whereas each component (the MCC and IMIS) just partially separates analyzed compounds.

It follows from (11) that even with $R_c = 0$ one can achieve a sufficient degree of separation of the compound peaks for which $R_d \geq 1$. But it should be born in mind that this is untrue for the chromatographic peaks with a small half width, since time is required to record each peak of a drift spectrum. Assuming that both peaks have equal t_R, only one drift spectrum peak can be recorded at a maximum of a chromatographic peak. The second drift spectrum peak will be recorded at a droop of a chromatographic profile. To avoid a considerable decrease in the amplitude of the drift spectra peaks, the width of the chromatographic peak and time for recording a drift spectrum should be comparable.

3.5. Time of setting readings (speed of response) of the GC-IMIS tandem

Speed of response is determined by the times of chromatographic analysis, ion separation and detection by the IMIS. The time of gas chromatographic analysis is determined by an absolute retention time of the last compound. When a right-angular concentration profile is fed to the input, time of setting the IMIS readings (t_s) is determined by time (t_i) required to transport a sample through the ionization chamber, time (t_t) of ions transportation through the ionization chamber to the ion collector, time (t_s) for setting electrometer readings. The values of t_i, t_t are 0.4 and 0.1 s, respectively, and are determined by the volume of the ionization and separation chambers, the flow rates of the input sample and drift gas. The value of t_e is about 0.2 s (up to 0.9 of the maximum value). Total time of one compound detection with the IMIS, t_s, is 0.7 s. The time required to detect two peaks with the preset values of U_c is determined by time of the first peak registration, t_{s1}, time, t_t, for transporting ions of the second peak through the separation chamber and time, t_{e2}, for setting the electrometer readings on detecting the second peak. A total time of recording two peaks is $t_{e12} \geq 1$ s.

4. Conclusion

As already mentioned, solving the problems of high-speed detection and identification of the vapors of explosives, chemical warfare agents and drugs in air with GC, one should consider the chromatographic column characteristics divided by analysis time along with high sensitivity and selectivity. The experimental values of separation power, N_t, registered in the range from 30 to 60 s^{-1}, degree of separation, R_t, (between 0.28–0.99 $s^{-1/2}$), number of possible peaks, $Z_t > 1$, at a length of a chromatogram obtained for the GC-IMIS testifies that the tandem holds much promise for performing express analysis of samples containing EAD.

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