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THERMODESORPTION THERMOIONIC SPECTROSCOPY:HIGH-SENSITIVE DETECTION OF TRACE AMOUNTS OF SYNTHETIC CANNABINOID AB-CHMINACA IN SMOKING MIXTURES

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Ушбу мақолада индазол ҳосилларидан бўлган синтетик каннабиноид AB-Chminaca ва у таркибига кирган турли матрицали мусодара қилинган чекилувчи аралашмаларнинг термодесорбциявий термоионлашув (сиртий ионлашув) спектрометрик (ТДТИС) ва ГХ/МС тадқиқот натижалари келтирилган. Иридий билан легирланган молибден оксиди термоэмиттери сиртида ҳаво атмосферасида термоион профиллари олинган, молекулаларнинг термоионлашув ва термодесорбциявий тавсифлари, аниқланиш чегаралари ва матрицаларнинг ТДТИ спектрга таъсири аниқланган. Услубнинг юқори танловчанлиги туфайли хроматографик ажратишсиз топилган юқори самарадорлик билан ионлашув (100 К/моль гача) ва аниқлашнинг ниҳоятда паст чегараси (0.1 пмольдан) ривожлантирилган услубни токсикология ва криминалистика лабораторияларида қўллаш истиқболини белгилайди.

В работе представлены результаты термодесорбционных термоионных (поверхностно-ионизационных) спектрометрических (ТДТИС) и ГХ/МС исследований синтетического каннабиноида AB-Chminaca (производного индазола) и конфискованных курительных смесей с содержанием каннабиноида на различных матрицах. На термоэмиттерах из оксида молибдена, легированного иридием в атмосфере воздуха, получены термоионные профили, определены термоионные и термодесорбционные характеристики молекул, пределы обнаружения и влияние матрицы на ТДТИ спектры. Установленные высокая эффективность ионизации (до 100 К/моль) и низкие пределы обнаружения (от 0.1 пмоль) без предварительного хроматографического разделения образцов, благодаря высокой селективности развиваемого метода, предполагает его применение в токсикологических и криминалистических лабораториях.

The results of thermodesorption thermoionic (surface-ionization) spectrometry (TDTIS) investigations of synthetic cannnabinoid AB-Chminaca (a derivative of indazole) and seized smoking mixtures on diverse matrixes have been presented. Thermoionic profiles have been obtained with thermoemitters from molybdenum oxide doped with iridium in air. Thermoionic and thermodesorption characteristics of molecules, limits of detection and matrix effect on TDTIS spectra have been defined. The high efficiency of ionization (up to 100 K/mol) and low limits of detection (from 0.1 pmol) have been determined without preliminary separation of samples and owing to high selectivity of the TDTIS method, which makes it possible its application in toxicological and forensic laboratories.

I. INTRODUCTION

At the end of the first decade of this century, relatively cheap new synthetic narcotic and psychotropic substances began to appear on illicit trafficking instead of “heavy” drugs (heroin, etc.) [1]. The appearence of synthetic cannabinoids (SC), derivatives of cathinone, piperazine and aminoindane, their predicted increase in illegal turnover as drugs of the “future” have changed the drug situation all over the world [1, 2]. They are actively introduced in the illegal market in the form of herbal smoking mixtures (Spice),

solutions for electronic cigarettes, powders for “bath salts” and tablets, gradually gaining “leading” positions [1]. Subsequently they were combined under one name - New psychoactive substances (NPS).

Among NPS, synthetic cannabinoids are most widespread. From cannabinoids synthesized for use in the treatment of neurodegenerative, immune, oncological and other diseases, JWH-018 as illegal drug was first discovered in Spice smoking mixtures in 2008 in Europe by forensic chemists [1]. SC sharply differ from classical cannabinoids (tetrahydrocannabinol) being in cannabis (hashish, marijuana, anasha) and have a variety of structures into which it is possible to make additional changes (designer drugs) [1]. Despite this, they have a feature that allows them to associate with cannabinoid receptors CB1 (discovered in 1990) or CB2 (discovered in 1993) located in the central nervous system and in human immune cells [2], respectively. Over the past 20 years the hundreds of SC preparations have been synthesized for medical purposes. These analogues also have an active effect on cannabinoid receptors and their physiological activity is determined by the affinity to the CB1 and CB2 centers. A great role in increasing the range of SC in illegal turnover is played by clandestine laboratories. Identification of these compounds causes considerable difficulties due to insufficient sensitivity of traditional methods of analysis, insignificant time of presence and constant expansion of their assortment at the consumption market of designer drugs, as well as frequent lack of standard samples. One of the factors of the popularity of NPS is the difficulty in detecting a fact of their use.

The constant expansion of the NPS assortment and growth in consumption requires development of new high-sensitive selective methods of analysis, which is one of the urgent social and forensic issues. Among the derivatives of indazole, the smoking mixtures with AB-Chminaca on illegal trafficking appeared first on marshmallow roots, damiana straw, mullein, chamomile and sage and in the form of powders [3]. To detect and identify this type of SC, the modern GC/MS, LC/MS-MS, HPLC-TOF-MS and NMR methods are currently used [4, 5]. There are reports about the cases of seizing and poisoning by them on the territory of Uzbekistan. Therefore, a highly sensitive detection of this type of drugs in forensic materials and products is an integral part of the struggle against their illicit trafficking.

AB-Chminaca is N-[(1S)-1-(Aminocarbonyl)-2-methylpropyl]-1-(cyclohexylmethyl)-1H-indazole-3-carboxyamide ($C_{20}H_{28}N_4O_2$ MW = 356) and is a nitrogen base. Therefore, its high ionization efficiency by TI should be expected.

The results of comparative studies of the analytical possibilities of chromato-mass spectrometric methods and thermodesorption thermionic spectroscopy for detection and identification of synthetic cannabinoid AB-Chminaca in forensic materials and products and studies of the matrix effect on the thermodesorption spectra have been presented.

II. EXPERIMENTAL

II.1. The device and experimental conditions

A modernized device “IK-Iskovich” was used to study synthetic cannabinoides by TDTIS [6, 7]. Briefly, the device consists of a temperature-programmed evaporator of the compound samples under analysis and a TI triode detector through which air moves from the evaporator to the detector. Evaporation takes place during heating of the cup by electric current and the molecules of analyties move with the air to the heated (up to T~700 K) surface of the emitter produced from Mo doped with Ir. The molecules are

adsorbed and while desorbing they can be ionized by the TI. Simultaneously with the dependence of temperature on time, the dependence of ion current on time is registered.

Emitter temperature is 700 K, airflow speed is 50 L/h, evaporator temperature scanning is linear with the rate of 10°C/s from room temperature to 500°C. GC-MS analysis was performed with an "Agilent-6890/5973N".

II.2. Samples and their preparation

In the experiments we used solutions of trace amounts of seized smoking mixtures (Spices), as well as micro-quantity of seized SC powders, provided by the laboratory of the Main Expert-Criminalistic Center of the Ministry of Internal Affairs of Uzbekistan. For the effect of plant matrixes of smoking mixtures on thermodesorption spectra, the solutions of commercial samples of chamomile and sage were prepared in toluene, acetonitrile and ethyl alcohol containing AB-Chminaca.

20–100 mg of the seized smoking mixture samples were dissolved in 1 ml of ethanol, acetonitrile and toluene. Then they were filtrated and 1–3 μl of the solution were put on the evaporator surface. The best results of extraction were achieved with the use of toluene and acetonitrile. It has been found that SCs are effectively dissolved in these solvents. It is established that the time required for this is minutes (2–5 minutes). Further increase in the time of holding the smoking mixture in the solvent leads to an insignificant (≈5–10%) increase in current in the thermodesorption spectrum.

The high selectivity of the TI method allows one to analyse the extracts without preliminary chromatographic separation.

III. RESULTS AND DISCUSSION

III.1. TDTIS analysis

A series of thermodesorption thermoionic spectra of synthetic cannabinoid AB-Chminaca for different amounts of substance is presented in Fig. 1. The thermodesorption spectrum has a maximum temperature T_{max}=200–220°C characteristic for indazole derivatives, it is relatively high as compared with natural cannabinoids (132–140°C) [8]. With increasing the amount of the substance deposited on the evaporator

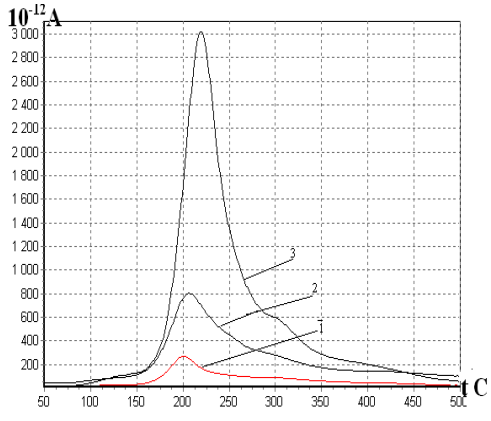


Fig. 1. TDTI spectra of AB-Chminaca: *1* – 25 ng, *2* – 50 ng, *3* – 100 ng.

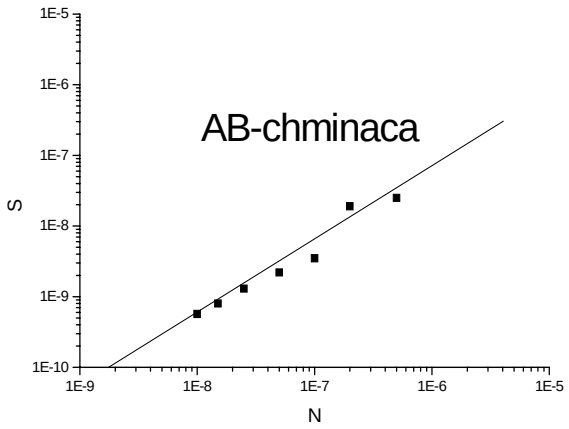


Fig. 2. Calibration curve of AB-Chminaca cannabinoid.

surface from 5 to 100 ng the maximum temperature T_{max} is shifted to high temperatures and this shift is 15–25°C. The ionization efficiency of AB-Chminaca molecules by TI determined from TDTI spectra is an order of 100 K/mole and is in agreement with that established for N-N heterocyclic compounds determined by the physical-chemical nature of the molecules and the electronegativity of the substituents.

The detection limits determined from the calibration curves are 1.7 pmol (Fig. 2) above the background level. The linear dynamic range is 2.5–3.0 orders of magnitude. The method allows fast (2–3 min) qualitative and quantitative analysis of SC in forensic materials be conducted with high sensitivity (from 0.5–1.0 ng/ml) as compared with the methods of GC/MS and HPLC-MS-MS.

III.2. GC/MS analysis

The samples of seized powders and smoking mixtures containing synthetic cannabinoids investigated by the TDTIS method were also studied by chromato-mass-spectrometry to validate the obtained results. The identification was carried out with the NIST-1 database of chromatograms and mass-spectra. For example, the chromatogram and the electron-impact mass-spectrum of the chamomile-based smoking mixture in which a synthetic cannabinoid AB-Chminaca was found are presented in Fig. 3 and Fig. 4, respectively.

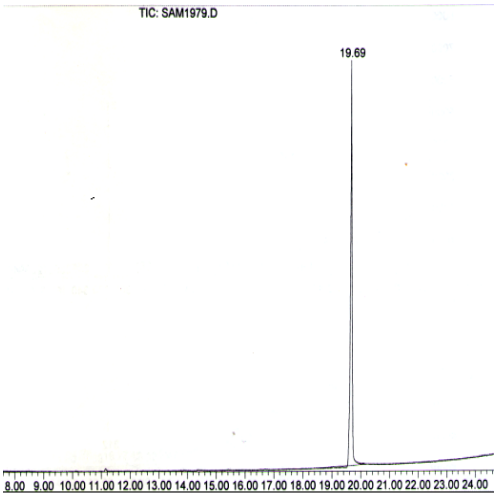


Fig. 3. Sample of chromatogram.

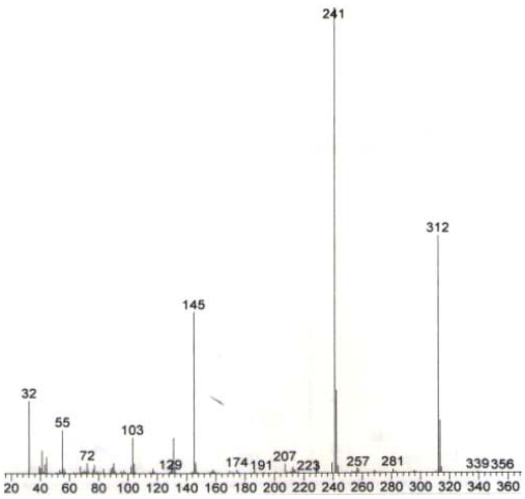


Fig. 4. Electron-impact mass-spectrum.

In the chromatogram (Fig. 3) the peak with the split vent time R_t = 19.69 min and in the mass-spectrum (Fig. 4) with the main ion line m/z=145, 241, 312 corresponds to AB-Chminaca cannabinoid.

IV. STUDY OF MATRIX EFFECT ON THERMODESORPTION SPECTRA

Straws of pharmacy chamomile and sage were studied to reveal the effect of plant matrixes on the thermodesorption spectra. In the pure chamomile spectrum (Fig. 5) there are four pronounced maximums corresponding to flavonoids for sublimation temperatures 120°C, 190°C, 285°C and 335°C; in the sage extract spectrum there are three temperature maximums T_{max} for 110°C, 245°C and 360°C.

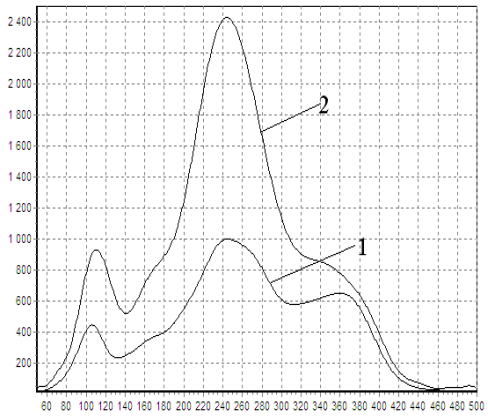


Fig. 5. TDSI profile of pharmacy Chamomile extract: *1* – 1 mkl, *2* – 2 mkl.

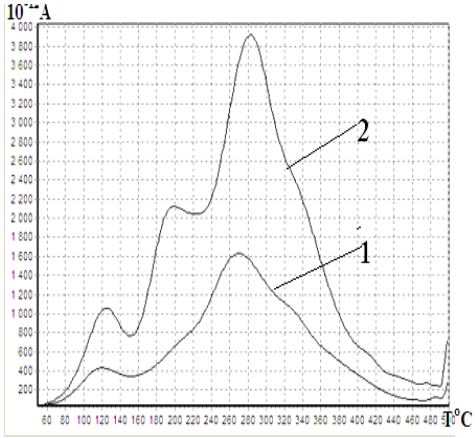


Fig. 6. The spectrum of pharmacy sage extract 1 g/ml: *1* – 1 mkl, *2* – 2 mkl.

It is seen that the spectra of chamomile and sage differ both in spectrum character and in quantitative parameters (area), which are evidence of the nature of flavonoids and their quantitative content. The temperature maximums of AB-Chminaca and flavonoids in the matrix extracts do not coincide. The temperature maximums in the TDTI spectra of seized smoking mixtures characteristic of chamomile and sage do not manifest themselves because of their small concentration.

V. CONCLUSION

The thermodesorption thermoionic (surface-ionization) spectroscopic studies of seized smoking mixtures and powders containing synthetic cannabinoid AB-Chminaca and their comparison with the chromate-mass-spectrometric investigations have demonstrated the high efficiency of ionization of synthetic cannabinoid molecules by TI. It has been established that TDTIS spectrum of synthetic cannabinoid AB-Chminaca significantly differs in temperature maximums (ΔT_{max}=55−70°C) of the thermodesorption spectra from classic cannabinoids.

The developed method, owing to high selectivity to nitrogen bases, allows one to analyse smoking mixtures without chromatographic separation since flavonoids containing in matrixes are ionized by TI with less efficiency (10^2–10^3 times). The results are evidence of perspectives of the developed method for application in practice of analytical laboratories of law-enforcement bodies.

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