Surface-ionization methods and devices of indication and identification of nitrogen-containing base molecules

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Abstract

The results of the development of methods and devices based on the effect of surface ionization (SI) and intended for the selective and sensitive registration and identification of the organic nitrogen base molecules in air and in mixtures of compounds for their chromatographic, ion mobility and mass-spectrometric analysis are presented. The main principles of the SI registration and identification of molecules are considered. The requirements that must be satisfied by devices implementing these principles are stated. The examples of the development of the effective and stable emitters, the simple-in-design diode SI detectors, the gas-chromatographic detectors, the SI gas analyzers of amines and the indicators and analyzers of narcotics including portable ones, SI ion mobility spectrometer and SI mass spectrometer are presented. They have a unique selectivity (up to 10^5–10^8 with respect to organic solvents) and ionization efficiency (up to ~$2 \cdot 10^{-1}$) of amines and their derivatives, including the degradation products of chemical warfare agents, tobacco alkoloids, triazine herbicides, narcotics and other abused medicinal preparations, as well as the sensitivity of up to 6 C/g and picogram level detection limits with a response dynamic range of 5–8 orders of magnitude. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Surface ionization detection; Detection, GC; Instrumentation; Opioids; Amines

1. Introduction — the phenomenon of surface ionization of organic compounds

The phenomenon of surface ionization (SI) consists in the formation of positive and negative ions in the course of thermal desorption of particles from the surface solid [1]. This kind of emission is in thermal equilibrium so that the evaporated particles (both ions and neutrals) exhibit a Boltzmann distribution in energy with a temperature equal to the temperature, T, of the solid involved.

The ionization mechanism is the isoenergetic transition of an electron from an adsorbed particle into a solid or vice versa. The particle can become a positive ion if its valent electron can occupy a free level in the valent band of the solid. Therefore the degree of SI:

$$\alpha = \nu^+ / \nu^\circ \tag{1}$$

where ν^+ is the flux of desorbed ions, ν° is the flux of desorbed neutral particles, is described by the well-known Saha–Lengmuir formula:

$$\alpha = A \exp\left[\frac{e(\varphi - V)}{kT} \right] \tag{2}$$

where A is the statistical mass ratio of the states of charged and neutral particles at the temperature T of

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the solid, e is the electron charge, φ is the electron work function and V is the ionization potential of the particle. So, SI is a highly selective process relative to V. For instance, if V of two particles differs by 1 eV, the ionization efficiency can vary up to 10^5 times. On the other hand, if V of a particle to be ionized satisfies the following condition:

$$e(\varphi - V) \gg kT \tag{3}$$

then the ionization efficiency of these particles is equal to unity, which cannot be reached by the methods of impact ionization.

The SI of atoms has been known since 1923; it is well studied and finds various applications [1].

The thermodesorption of multiatomic ions of specific organic compounds has been found comparatively recently [2]. The thermal equilibrium mechanism of many-atomic ion desorption and the possibility of using the Saha–Lengmur formula to describe the many-atomic ion ionization has been experimentally proven [3,4]. The general regularities and peculiarities of SI for molecules of various classes of organic and bioorganic compounds have been established [5,6].

The molecules can undergo a chemical transformation on the surface, not only original particles but also the products of their heterogeneous transformations can desorb as ions. If molecules on the surface of a solid are transformed into i species of new particles, then the incident flux can be formally represented as consisting of i effective fluxes ν_i, each of them producing particles of one species only. Now the relation between ν_i and ν, the flux of molecules going to the surface, can be written in the form:

$$\nu_i(T) = \gamma_i(T)\nu \tag{4}$$

where γ_i is the total reaction yield determining the concentration of the given i particles on the surface. γ_i depends not only on the rate constant of the corresponding chemical reaction, but also on the rate constants of all the other processes in which the original molecules and the particles formed from them participate in the adsorbed state [5].

The current density:

$$j_i = e\nu_i^+ = e\nu\beta_i\gamma_i \tag{5}$$

where $\beta_i = \nu_i^+/\nu_i$ is the ionization coefficient con-

nected with α_i by the relation $\beta_i = \alpha_i/(1 + \alpha_i)$, so that the expression (5) for the current densities reduces to the form:

$$j_i(T) = \frac{e\nu\gamma_i(T)}{1 + A_i^{-1}\exp\left[\dfrac{e(V_i - \varphi)}{kT}\right]} \tag{6}$$

Thus, the dependence of ion current on T, in this case, is defined not only by the dependence of $\beta_i(T)$, but also by that of $\gamma_i(T)$. If condition (3) is satisfied — the case of 'light' ionization — then the exponential term in Eq. (6) can be neglected and we have:

$$j_i \approx e\nu\gamma_i \tag{7}$$

In the case of 'hard' ionization when the following condition is valid:

$$e(V_i - \varphi) \gg kT \tag{8}$$

then the unity in the denominator of Eq. (6) can be neglected and we have:

$$j_i = e\nu A\gamma_i(T)\exp\left[\frac{e(\varphi - V_i)}{kT}\right] \tag{9}$$

By now, the SI of over 500 organic and bioorganic compounds has been studied mass spectrometrically for the emitters from various materials [5–7]. These compounds are amines, hydrazines and their different derivatives including different physiologically active substances [2,5,8,9], arsines and phosphines [10], some hydrocarbons [7,11,12], some oxygen-containing compounds [2,7], organometallic [7] and benzoyl-containing ones [13] and quaternary amine salts [14]. It has been found that the molecules of organic solvents (ketones, aldehydes, spirits, simplest hydrocarbons) and of simple gases (H_2, N_2, CO_2, CO, H_2O) cannot be practically ionized by SI.

Nitrogen bases — amines, hydrazines and their derivatives including a great number of physiologically active (narcotic and psychotropic) substances are ionized more effectively by SI. Thus, almost each second–fifth molecule of tertiary amines and their derivatives incident onto the surface leads to the ion desorption. The main regularities and peculiarities of SI for nitrogen bases have been found and the simple rules of the ion formation have been formulated allowing the prediction of the ion composition in the SI mass spectra of amines and their derivatives and the evaluation of the corresponding ion current

densities [5,6,8]. These rules stem from the high selectivity of SI with respect to the ionization potential of the particles under study; from the fact that the formation of bond-saturated ions, which in the case of amines can be represented as having a quadrivalent, positively charged hybridized nitrogen atom, is an energetically preferable process; finally from the dependence of the V of the particles to be ionized on the electronegativity of the substituents.

So, amines are adsorbed by establishing a coordination bond with an adsorbent via a lone pair of electrons of the nitrogen atom. This results in weakening of the β-bonds relative to nitrogen. The decay of these bonds leads to the formation of $(M-H)_\beta$ and $(M-R_i)_\beta$ radicals on the heated surface of the emitter. Such particles, as shown by measurements of their mean lifetimes on the emitter surface, reside for a comparatively long time on it ($\sim 10^{-3}$ s at $T \sim 1000$ K for oxidized tungsten [15]), attain a thermal and charge equilibrium with the emitter surface and are ionized by the SI mechanism when desorbing. The yield of these reactions can be close to unity for the ionization on the surface of oxidized W, the $(M-H)_\beta^+$ and $(M-R_i)_\beta^+$ current densities can be up to ~ 5 A/Torr cm^2 for tertiary amines (1 Torr = 133.322 Pa).

Before the amine ionization, the molecule dehydrogenization on the emitter can occur. The ionization of the compounds, thus, can form $(M-H-2nH)^+$ and $(M-R_i-2nH)^+$ ions.

The ionization of primary and secondary amines always reveals stable and reproducible $(M+H)^+$ ions originating from the ionization of the $(M+H)$ complexes which are produced in the autoassociation of original molecules at the surface [2,16]. $(M+H)^+$ ions can be observed also in the ionization of tertiary amines. Complexation is favored, in this case, by the presence of a residual gas of water vapor or other protophobic compounds [6,16] in the mass spectrometer.

It is important to note that SI is one of a few methods of ion formation capable of working in air. The SI mass spectra of organic compounds obtained in vacuo and in air are practically the same and consist mainly of quasi-molecular ions of $(M+H)^+$, $(M-H)_\beta^+$ and $(M-R_i)_\beta^+$ [17].

Thus, the SI phenomenon is unique, characterized by the high ionization efficiency and selectivity of nitrogen-containing organic bases, and capable of working in a vacuum and in an air atmosphere. This makes it possible to use SI for the sensitive registration and analysis of the trace amounts of these bases in natural, technological and bioorganic complex mixtures.

The results of the developments of different SI methods and devices allowing the registration and identification of nitrogen base molecules with the selectivity and sensitivity non-accessible for other methods are given below. Both the results of unpublished works and a brief review of papers, published mainly in Russian, are presented.

2. Experimental

All emitters, detectors, gas analyzers and drift spectrometers mentioned below were manufactured in the laboratory. Metals for the emitters were produced in Russia (UzKTJM, Chirchik; OAO, Plant of non-ferrous metals, Ekaterinburg, Russia). Single molybdenum crystals were grown in the laboratory by zone melting [18]. The methods of manufacturing the emitters and their thermal treatment and oxidization are described in detail in [18,25,33].

The characteristics of the detectors and ion sources for ion mobility spectrometry (IMS) were studied both for the mode of their continuous operation when the detector is fed by the air with the given concentration of amines (Voykov Plant, Moscow, Russia; Pierce, Rockford, IL, USA), and for the chromatographic mode with the use of chromatographs LKhM-8MD, model 3, Tsvet-500M, model 550 (OKBA, Dzerjinsk, Russia), Pay-Unicam, series 104 and HP-5890 (Hewlett-Packard, Wilmington, DE, USA) equipped with a glass column packed with 5% polyethyleneglycol +0.5% Na_3PO_4 or 4% Apiezon +1% KOH on Chromosorb G AW or with a DB-5 ms (J&W, Folsom, CA, USA) capillary columns (30 m×0.32 mm inner diameter, 0.5 μm in film thickness) [21–24].

The design of drift spectrometers is given in detail in Ref. [19], and that of IMS drift tube in Ref. [24].

In the mass spectrometric studies a modernized magnetic mass spectrometer MI-1201V (NPO Elektron, Sumy, Russia) with an emitter from oxidized W wire was used. The samples of narcotic CAS prepa-

rations (UNDP/UNIDO) and urine extracts (Bureau of Forensic-Medicine Expertise, Tashkent, Usbekistan) were evaporated from the Knudsen cell with a platinum heater. For the comparison SI-MS with electron impact (EI) MS, the samples were studied also by a chromato–mass spectrometer HP-6890 (Hewlett-Packard, UNDP/UNIDO).

3. Results and discussion

3.1. Ion emitters

The ionization efficiency is determined not only by the properties of particles to be ionized, but also by thermoemissive and catalytic properties of the surface, where the ionization occurs. This can be achieved if the positive ion emitters possess a high work function and certain catalytic properties (dissociation reactions with the formation of particles having a low ionization potential), as well as if both these characteristics are stable in time at emission temperatures and not affected by the attack of the organics in question.

The SI has been studied for the emitters from different refractory metals (W, Mo, Ni, Re, Pt, Ir) and their oxides (or metal–oxygen systems) [2,6,7,25]. Their thermoemissive properties are known [1,6,26]. Among the metals, the metals of the platinum group (up to ~5.8 eV) and Re (up to 5.6 eV) have the higher work function. However, the dissociative adsorption of organic compounds results in the formation, on these metals, of a monolayer of carbon with the graphite structure lowering the work function up to $\varphi = 4.5$ eV and inhibiting the dissociation of the adsorbed molecules [28]. So these metals are not used as emitters to ionize organic compounds in a vacuum. An exception is an emitter from Ir with a carbon monolayer of the graphite structure which is used for the SI mass-spectrometric analysis of quaternary ammonium salts when only the whole cations of quaternary amines are desorbed as ions [14].

Oxides of refractory metals have the highest work function and SI is more effective for them. The methods of their production and the properties of some of them are given in Table 1. The emitters from oxidized Re have the greater work function. But they are unstable and 'poisoned' for a short time when there are organic vapors. The products of the organic compound decomposition reduce the surface layer of oxide to metal and further cover it by carbon, which decreases the work function (up to $\Delta\varphi \sim 1.5$–2.0 eV) and ion emission [25,29]. To

Table 1
Thermoemissive properties of emitters from oxidized metals

Material	Oxidation conditions	Electron emission		Ion emission φ_{max} (eV)	Reference
		φ_{min} (eV)	χ (eV/deg)		
W (wire)	$T = 1100$ K $p = 0.2$ Torr $t = 10$–15 min	6.00 ± 0.08 800 K	$2.5 \cdot 10^{-4}$ 800–1300 K	6.7–6.8	[4]
W (ribbon)	$T = 1000$ K $p = 1$–2 Torr $t = 30$–40 min	6.12 ± 0.08	800–1300 K $3 \cdot 10^{-4}$	6.5	[6]
Re (wire)	$T = 1000$–1050 K $p = 1$–2 Torr $t =$ several hours	6.5 1000–1200 K	$1 \cdot 10^{-4}$	7.0	[29]
Mo (wire)	$T = 750$ K $p = 0.5$ Torr $t = 45$–60 min or $p = 760$ Torr $t = 15$–20 min	6.0	Depends on oxidation temperature	6.5	[6]

operate relatively stably, the surface of Re must be continuously oxidized, for example, by continuous leak-in of oxygen up to pressure of $\sim 10^{-3}$ Pa [27,29]. However, in this case also, the alteration of the emitter temperature T or the molecule flow to the surface can result in unstable emission. Therefore in Refs. [7,30], the SI mass-spectra of organic compounds are presented for a relatively high fixed temperature T of the Re emitter. This not only lessens the possibilities of the SI-MS, but also can lead to ambiguous results when analyzing different compounds because the 'poisoning' of the emitter by different compounds can differ.

The best (effective and stable) emitters to operate under vacuum conditions are those from W with a 'thick' layer (up to $\sim \mu$m) of oxides on the surface. In case of oxidized W, in contrast with oxidized Re, the W oxidization by oxygen from the oxide bulk prevents from the reducing of the surface layer of oxides by the products of the organic compound decomposition. Since the oxidization rate is higher than the rates of the oxide reducing reaction, the surface properties are stable practically up to the complete exhaustion of the 'thick' layer of oxides by oxygen. In the case of the triethylamine molecule SI, the emitter properties are stable up to a dose of $5 \cdot 10^3$ L [6,25].

The emitters from Mo wire (up to $T \leq 750$ K) and metals of the platinum group are used to operate in the air atmosphere [25,31,32]. They demonstrate the high efficiency of the nitrogen base ionization, and the devices with these emitters have a high sensitivity. However, they are not sufficiently stable owing to the alteration of the emissive and catalytic properties of the emitter surface in time and in process of the interaction of the flows of substances under analysis with the surface.

The best (effective and stable) emitters to operate in air are the emitters from single crystalline Mo doped with ($\sim$1%, v/v) elements of the platinum group [33]. They are not less effective than the emitters from the wires of Mo, Pt, Ir but essentially more stable and have a lower level of noise and background current.

3.2. Surface ionization devices with integral system of recording desorbed ions

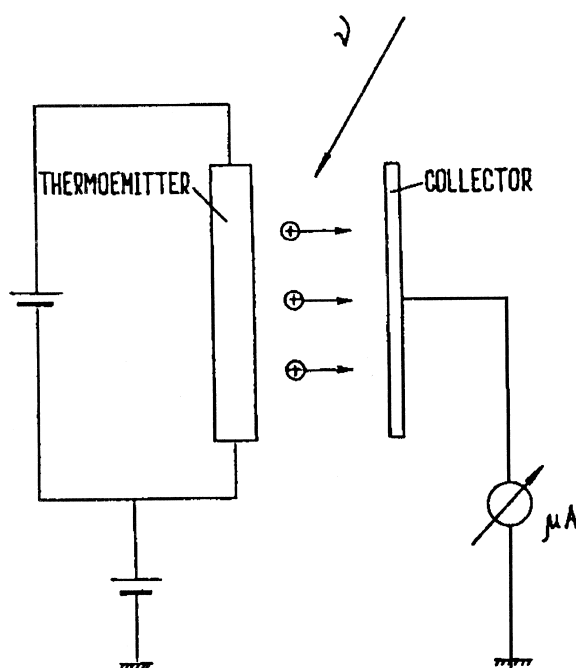The operation principle of SI detector is rather

Fig. 1. Operation principle of the surface ionization detector.

simple (Fig. 1). This is a diode, the heated anode of which is an emitter and the cathode is an ion collector. When passing a mixture under analysis through the diode, the molecules incident onto the emitter surface can be desorbed as ions that move under the electrical field to the collector for their recording.

For the SI detector, the ionization efficiency according to Lovelock is defined as follows:

$$L = \frac{\nu_+}{\nu_M} \tag{10}$$

where ν_+ is the number of the molecules ionized in the detector, ν_M is the total flow of molecules passing through the detector [21]. Therefore, from Eq. (5) we obtain:

$$L = \frac{\nu \sum_i \gamma_i(T)\beta_i(T)}{\nu_M} = \eta \beta_M \tag{11}$$

where $\eta = \nu/\nu_M$ is the coefficient of using the substance in the detector, showing what part of the total flow of the molecules reaches the emitter surface. It is defined by the detector design. The

value of $\beta_M = \Sigma_i \gamma_i \beta_i$ characterizes the ionization efficiency of molecules of a given substance on a given emitter and is defined by the emitter properties for each species of molecules. SI of triethylamine molecules on oxidized Mo wire occurs with $\beta_M \geqslant 0.08$ [25], and for organic solvents (hydrocarbons, spirits, aldehydes, ketones, ethers) $\beta_M \lesssim 10^{-6}$–10^{-8}. The background current of the SI detector is defined mainly by the current of Na^+ and K^+ ions because Na and K are always present in any emitter material.

In design, the SI detectors can have practically any size and shape depending on the problems to be solved. The large values of β_M make it possible to obtain the necessary values of L even for the small values of η. The first SI detectors were developed for the SI gas analyzers, 'Valdai' intended for the continuous control of alkylamines in industrial premises [31,34]. Even for $\eta \sim 10^{-4}$ the detection sensitivity of these detectors with an emitter as a spiral from oxidized Mo wire was sufficiently higher than that necessary to register the accepted limits of di- and triethylamines in air.

3.2.1. Surface ionization detectors for gas chromatography

In Ref. [21] the main principles were formulated to design the SI diode detectors with maximal η, as well as, for the first time, an SI detection (SID) system was designed and produced for gas chromatography with the best (until now) characteristics in ionization efficiency and sensitivity.

In design, the detector was a diode of cylindrical symmetry with an emitter as a spiral from oxidized Mo wire placed inside a cylindrical collector. Inside the spiral there was a current carrying lead occupying most of the internal spiral volume. It was found experimentally that the ratio of the spiral length to the gap between the electrodes is $l/d \geqslant 10$ ensuring the maximal value of η. The working volume of the detector was 0.2 cm^3 and allowed the use of the detector in chromatographs with any columns. The detector was tested by using chromatographs LKhM-8MD, model 3 and Pay-Unicam, series 104 where it was connected parallel to a flame-ionization detection (FID) system. Over 20 amines were studied and the following characteristics of the detector were obtained [21,22]. (1) Ionization efficiency L is from

$2 \cdot 10^{-2}$ to $2 \cdot 10^{-1}$ for tertiary alkylamines; $\sim 10^{-3}$–10^{-2} for secondaries; $\sim 10^{-4}$–10^{-5} for primaries; (2) the linear range is $\sim 10^{-6}$–10^{-8}; (3) background current and noise level are $\sim 10^{-11}$ and 10^{-13} A, respectively; (4) degree of selectivity relative to organic solvents (hydrocarbons, spirits, ketones) is $\sim 10^5$–10^8 and (5) the threshold sensitivity for tertiary amines is $\sim 10^{-14}$–$5 \cdot 10^{-15}$ g/s.

The ratio of SID and FID signals is $\sim 10^3$–10^4 for tertiary amines, $\sim 10^2$ for secondaries, ~ 10 for primaries and 10^{-3}–10^{-5} for hydrocarbons. This characteristics internal class selectivity of SI allowed a simple method to detect the nature of a functional group containing the nitrogen atom when analyzing mixtures of complex amines according to SID/FID signals [22].

The high ionization efficiency L of tertiary amines, essentially greater than that of all classes of organic compounds, makes it possible to propose a method of equisensitive detection with SID of any organic compounds in mixtures undergoing chromatographic separation [35]. If one adds a tertiary alkylamine, at a certain concentration, to the carrier gas passing through a chromatograph, then its vapor entering the SID will produce a high stable background current, its magnitude being proportional to the amine concentration in the carrier gas. For instance, when the carrier gas contains $\sim 10^{-4}$ mg/l of triethylamine, the ion current in the SID will be $\sim 10^{-6}$ A. When a mixture to be analyzed is injected into a chromatograph and undergoes separation in the column into individual components, the concentration of carrier gas and of the ternary amine in the zone corresponding to each component of the mixture will be inversely proportional to the volume concentration of the mixture. Therefore, as each component passes through the detector, one will observe a decrease of the background current which is proportional to the volume concentration of the component in question. Note that since the L of tertiary amines exceeds those of all classes of organic compounds, the decrease of the current will not depend on the actual composition of the mixture, which means that the method is equally sensitive to all organic compounds.

Later as a 'new' detector without reference to Ref. [21,22], an SID system manufactured by the modification of a thermoionic standard detector from

Shimadzu was proposed, where a Pt wire spiral was used as an emitter [36]. The great characteristics of SID close to those obtained in [21,22] were demonstrated. The somewhat lower sensitivity and ionization efficiency than those in Ref. [21] are explained by the lower value of η, and the linear dynamic range of 2 orders less is due to the above-indicated disadvantages of the Pt emitters.

The high characteristics of SID are used to analyze different nitrogen bases [37]. Moreover, the chromatographs 'Tsvet' and 'Shimadzu' with SID systems were put into production [38]. However, a common disadvantage of the above-described SID systems is the insufficient stability of their operation due to, mainly, the unstable properties of the wire emitters. As indicated in Refs. [21,36], there is sufficiently high reproducibility of the detectors for multiple injection over a work-day of the trace amounts of amine under analysis; however, the operation of the detectors can be unstable, for different days and particularly for the analysis of complex mixtures of compounds. Therefore in these cases, it is necessary to make an additional calibration of the detectors.

Largely without these disadvantages is an SID system with an emitter of indirect heating made of a Mo single crystal doped by Ir [23] . Its design is given schematically in Fig. 2. The design ensures a high η, the isotropy of T along the emitter length. The availability of a thermocouple connected in back-coupling of a power stabiliser ensures a constant temperature of the emitter, not depending on oscillation of flows of gas carriers and air and on their ratio or a type of gas carriers. And finally, the stability of the emissive and catalytic properties of the used emitter ensures the reproducibility within 3–4% for tertiary amines and up to 5% for secondaries and primaries not only for a day, as in [21,36], but also for several months of operation. The detector has the highest characteristics in ionization efficiency, selectivity and sensitivity. For example, for tripropilamine $L = 1.8 \cdot 10^{-1}$, the sensitivity is $K = 6$ C/g, the linear range is $\sim 10^{8}$, the selectivity relative to organic solvents is $\sim 10^{6} – 10^{8}$. Therefore, this design of the diode SID system with the indicated emitter of one or other modification has used to develop the SI gas analyzers and ion sources for ion mobility spectrometers.
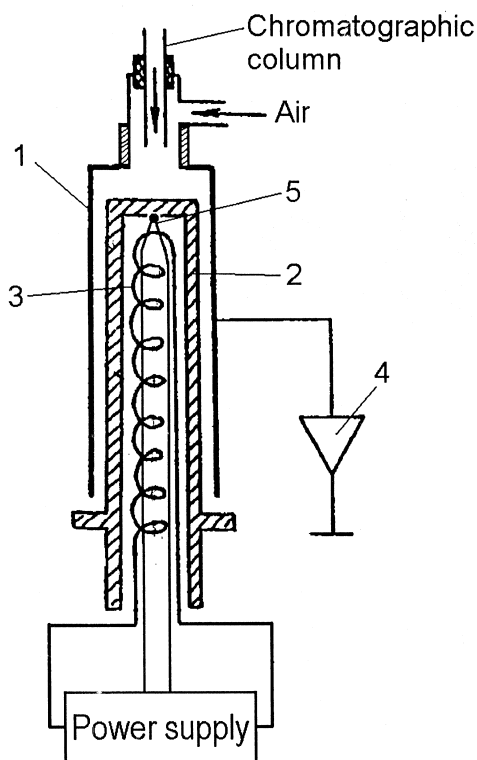

Fig. 2. Design scheme of the SID system with an indirect heating emitter from monocrystalline Mo doped by Ir. 1 = Collector; 2 = emitter (6 mm in diameter, 38 mm in length); 3 = nichrome heater; 4 = charge amplifier; 5 = thermocouple.

3.2.2. Surface ionization portable gas analyzer

The unique selectivity and sensitivity of SID are used to develop SI gas analyzers to detect the trace amounts of amines and their derivatives in gas–air mixtures [40]. A photograph of one of models of the portable gas analyzer is shown in Fig. 3. Their mass is 3 kg. The SID system is located in a removable probe through which the air passes at a speed of 50 l/h. When there are molecules of nitrogen bases in the air the SID system registers the ion current proportional to their concentration. The power supply of the SID system is made by a special unit. The latter can be connected both with the power network and with a self-contained battery of 12 V. There is a digit indication of the ion current, as well as sound and light signaling for the given level of the ion current (or the given level of the concentration of amine in the air). The gas analyzer allows the
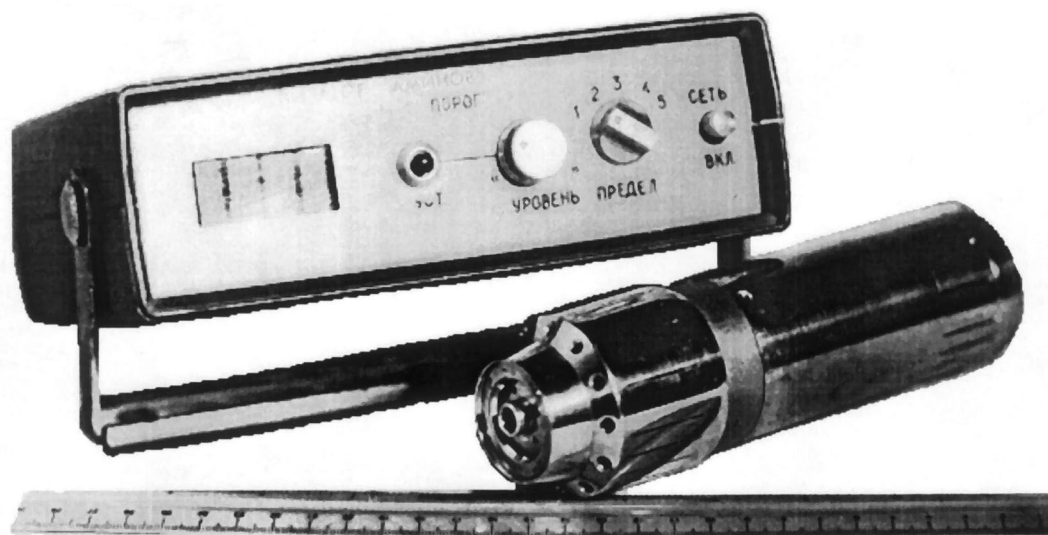
Fig. 3. Portable SI gas analyzer.

registration, for example, of tertiary amines in the air with a concentration of $\sim 10^{-10}$ g/l.

The fields of the SI gas analyzer application are chemical sensors for monitoring of the environment and for providing of medical standards on working places connected with the production or use of amines; examination of polymer substances on the subject of their conformity with medical-sanitary standards of amine gas liberation under mechanical actions, heating, long-term preservation and so on; in leak detecting to test the leak-proofness of large volumes and superlong objects (pipe-lines, cable sheaths) [41].

3.3. Surface ionization indicator of narcotics

Narcotics, psychotropic substances and many other abused medicinal preparations have very low vapors pressures at room temperature. So for their registration and analysis, for example, by the IMS method, the sample selectors are used. The microparticles of narcotics are collected by passing the air through the filters of the sample selector or by wiping the places where narcotics can be. Further the filters are placed into the special heaters where the narcotics particles are evaporated from the filters at $T \sim 250°C$ and vapors enter IMS. When this heater is connected to the above-described gas analyzer, SID

registers the integral current of ions from the ionization of all nitrogen bases evaporated from the filter at $T \sim 250°C$. The diode type detector does not permit the identification of specific amines against a background of other ones. Therefore, for the registration of nitrogen bases volatile at room temperature, for example, to detect narcotics and other abused medicinal preparations in urine, blood or postmortem materials, a model of an SI indicator consisting of the above-described SI gas analyzer and a device with a temperature-programmed evaporator to analyze the samples was developed. This indicator is given schematically in Fig. 4.

The microamounts of the extracted sample solutions are put on the central part of the surface of the graphite-covered metallic band (sample evaporator). By applying the electric current, the band is heated according to the given mode of the dependence $T(t)$.

Evaporated from the band, the molecules of the sample enter the SID system with the air flow where nitrogen bases can be effectively ionized. Synchronous with the dependence $T(t)$, the dependence of ion current on time $I(t)$ is fixed.

The dependencies $T(t)$ and $I(t)$ for the analysis of the trace amounts of opioids and synthetic narcotics are presented in Fig. 5. It is seen that the dependencies $I(t)$ are characteristic of each of the compounds: maximums and shapes of $I(T)$ differ visibly. The
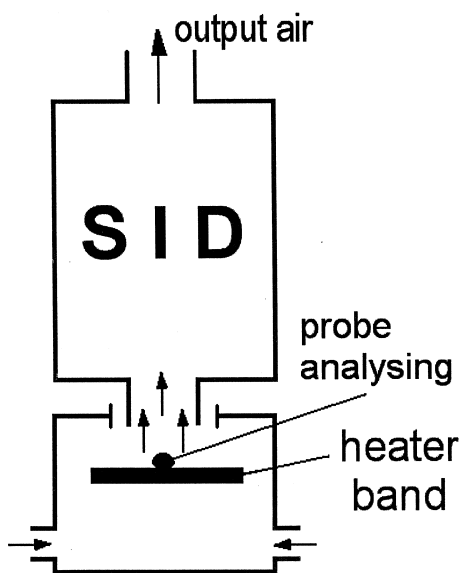
Fig. 4. Scheme of the SI indicator of narcotics.

wider peak $I(T)$ of illicit heroine can be caused, for example, by ~8% acethylmorphine and ~10% acetylcodeine available in heroine as impurities.

The high sensitivity of SID allows us to fix with confidence the dependence $I(t)$ above the background level (~$5 \cdot 10^{-11}$ A) for the amounts of opioids in the sample under analysis ~$5 \cdot 10^{-10}$ g (Fig. 5). Since the noise level of the SI indicator is ~$5 \cdot 10^{-13}$ A, then the detection limit can be up to ~$5 \cdot 10^{-12}$ g.

For the possibilities of the indicator to be tested, the comparative analysis of urine of heroine users has been made by GC–MS HP-6890 and by the SI indicator. The dependence $I(T)$ is presented in Fig. 6 for the analysis of some samples. Sample No. 8 was identified reliably by GC–EI-MS as having the metabolism products of illicit heroine. Samples Nos. 25 and 11 could not be identified by GC–MS HP-6890 owing to the lack of the device sensitivity. It is seen from Fig. 6 that the SI indicator fixes reliably, in samples Nos. 25 and 11, the nitrogen bases that
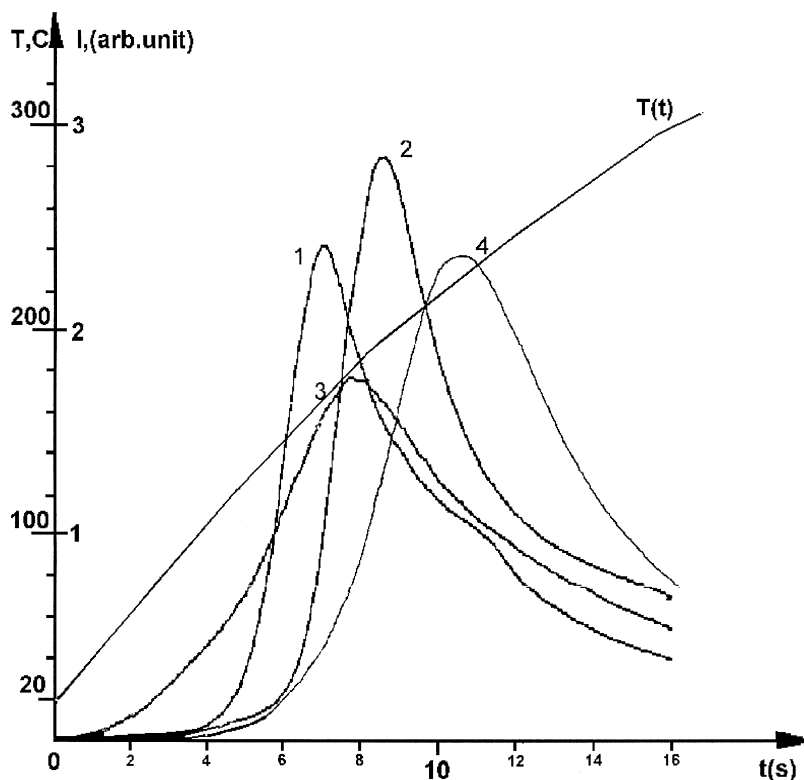

Fig. 5. Desorption spectra of different opioids. 1 = Codeine; 2 = morphine; 3 = illicit heroine in an amount of ~1.0 ng in the probe, ion current at maximum is ~$2 \cdot 10^{-10}$ A; 4 = methamphetamine.
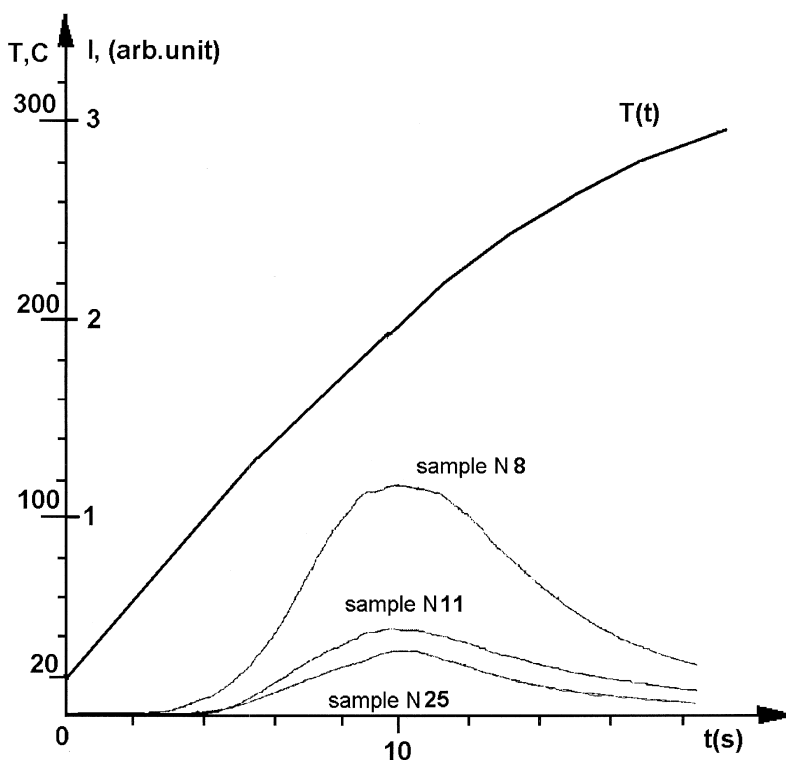
Fig. 6. Desorption spectra of the urine samples of heroine users.

are evaporated from the evaporator surface at the same T as opioids of sample No. 8, but in the amount several times less than in sample No. 8. The preliminary estimations show that sample No. 8 has 300 ng/ml of opioids, samples Nos. 25 and 11 have 75 and 65 ng/ml, respectively. Thus, the results of these first experiments indicate the essentially higher sensitivity of the narcotic registration by this simple-in-design and inexpensive SI devices as compared to HP-5890. The tradeoff is that the SI indicator is a selective indicator of narcotics, while GC–MS is a universal method of analysis with essentially greater reliability than the method proposed. (The comparison of SI-MS and EI-MS will be made below). However, the reliability of the analysis by the SI indicator is close to the results of color thin-layer chromatography, and the sensitivity is 10^2 times and more higher. Therefore, it can be supposed that this method and device will find application in narcological and toxicological laboratories not only for the

detection of narcotics in samples but also in other physiologically active abused medicinal preparations.

3.3. Surface ionization ion mobility spectrometry

The use of the SI ion sources in the IMS analysis of nitrogen bases has the essential advantages as compared to other ionization methods not only owing to the unique selectivity and efficiency SI:

1. only one-dimensional and one-charged ions of known composition are formed by SI;
2. there is no electron injection, i.e. there are no conditions causing additional ionization of molecules in gases;
3. the particle with the low energy of the formation (the low ionization potential) are ionized by SI, so in the gaseous phase there are no ion–molecule reactions with the charge exchange.

The indicated advantages were demonstrated when a SI source was designed and constructed for IMS

[24]. Triethylamine was employed to study the behavior of the ionization source under different source conditions and gaseous environments. The ion mobility spectra of triethylamine consist of MS identified peaks of the ions $(M-CH_3)_\beta^+$, $(M-H)_\beta^+$, $(M+H)^+$ really appearing at the high concentration of amine, cluster ions $(M-CH_3)^+M_n$, $(M-H)^+M_m$ and $(M+H)^+M_k$. Amines (including the degradation products of chemical warfare agents), tobacco alkaloids and triazine herbicides were also studied by GC–SI-IMS. The picogram level detection limits were achieved for target compounds with a response dynamic range of five orders of magnitude. For example, the calibration of nicotine and major degradation products of VX- or V-type chemical warfare agents is shown in Fig. 7. The slope is 0.95 for diethylethanolamine (DEEA) and 0.87 for diisopropylaminoethanol (DIPAE), and 0.8 for nicotine.

The calculated detection limit is $3.7 \cdot 10^{-14}$ g/s for DEEA, $3.9 \cdot 10^{-14}$ g/s for DIPAE and $2.2 \cdot 10^{-13}$ g/s for nicotine. The dynamic range is several orders of a magnitude greater than that of the ^{63}Ni source, and since the SI process does not involve gas-phase ion–molecule reactions, the IMS tube can be constructed without a 'reaction region' reducing the length of the tube by 30%.

3.4. Surface ionization drift spectrometer — portable gas analyzer with separation of ions by their mobility

In contrast to traditional method of ion separation by drift velocity $\nu = K_i E$ in the constant longitudinal electric field E, a new separation method has been used [19,20,39]. It is based on the dependence of ion mobility K_i on the value of the electric field $K_i(E)$.
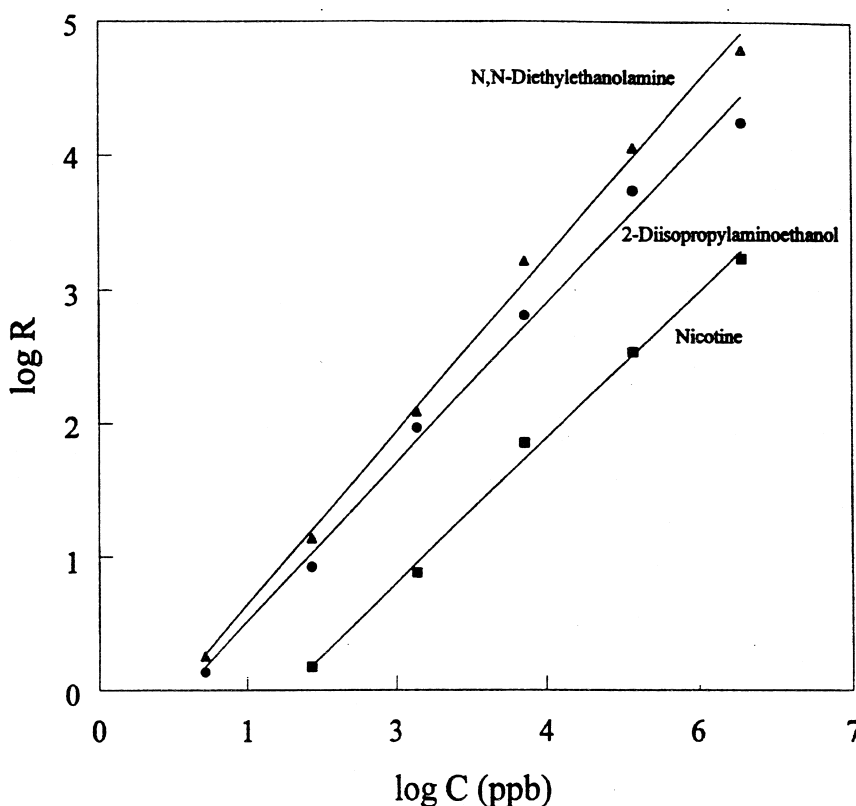

Fig. 7. Calibration curve of nicotine, 2-(diisopropylamino) ethanol and N,N-diethylethanol amine. GC conditions: oven temperature, 200°C; injector temperature, 250°C; IMS conditions: tube temperature, 192°C, drift gas flow, 1.2 l/min [24].
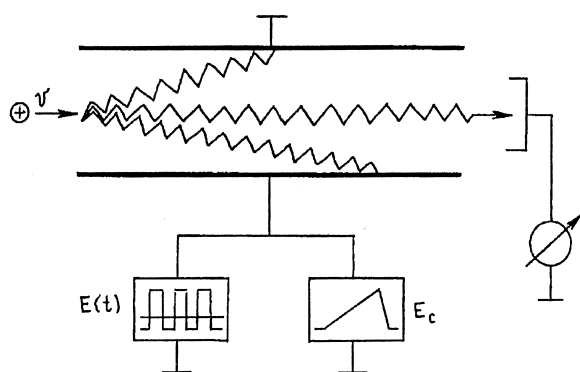
Fig. 8. Scheme of ion separation in a drift spectrometer.

The idea of the method is illustrated in Fig. 8. If ions with the gas-carrier stream are directed to the narrow gap between two plates and periodic voltage pulses of asymmetric polarity are applied to these plates to create strong electric fields $E(t)$ between them, then the ions will oscillate in transversal direction during their motion along the plates. Since ions of various species will move along different trajectories, only ions whose average deviation of trajectory in the transversal direction during the total period of oscillation of the high-frequency field is equal to zero will pass through the capacitor gap. The trajectories of other ion species may be straightened either changing the relative pulse duration of the high-frequency field or using the constant compensating electric field E_c. Therefore, by means of the consecutive straightening of the trajectories of different species ions, for example, using sawtooth voltage $E_c(t)$, it is possible to record the drift spectra.

This principle is the basis of creation of the small-sized gas analyzer — the drift spectrometer [39]. Ion separation occurs in the gap with a width of 0.5 mm between two metal plates with dimensions of 0.5×1.5 cm under high-frequency ($F = 2$ MHz) voltage with an amplitude of 1.8 KV. Total mass of the drift spectrometer is <2 kg.

The drift spectrometer has two main modes of operation:
1. tracking in real time for the content and change of the concrete substance in gas–air mixture under analysis;
2. recording of total spectrum of ion mixture.

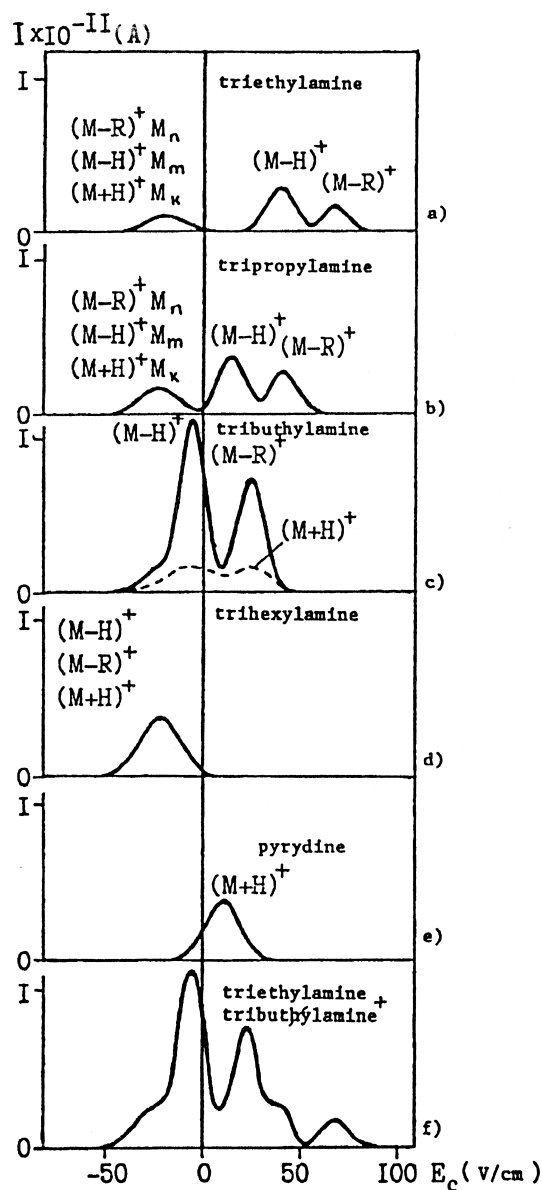Fig. 9 shows complete drift spectra for series of

Fig. 9. Drift spectra of some amines.

individual tertiary amines and of mixture of triethylamine and tributylamine. MS identification of ion composition of each line of the drift spectra has confirmed the efficiency of this separation method. The drift spectra consist of well resolved lines of ions $(M-H)_\beta^+$ and $(M-R_i)_\beta^+$ and of the lines of unresolved complex (cluster) ions $(M-H)_\beta^+ M_m$, $(M-R_i)_\beta^+ M_n$, $(M+H)^+ M_k$, where m, n and k are

integral numbers. The detection threshold of tertiary amines is of $\sim 10^{-10}$ g/l.

3.5. Surface ionization mass spectrometry

The SI mass spectra of morphine, codeine and heroine are presented in Fig. 10. They obey the regularities of the ion formation by SI [6,8] from the lines of quasimolecular ions $(M-H)_\beta^+$, $(M-H-2nH)_\beta^+$ and $(M-R_i)^+$. All the ions can be presented as the stable valency-saturated ions with a quadrivalent positively charged atom of nitrogen with the sp^2-hybrid orbitals. So, despite the availability, in the cycle, of a few β-bonds relative to the nitrogen atom, the decay of only two of them results in the formation of such ions. These are the quasimolecular ions $(M-H)_\beta^+$ and $(M-H-2nH)_\beta^+$ obtained by the elimination of the hydrogen atom from the piperidine ring or from the methyl radical (their intensity is 40% in the mass-spectra of codeine and morphine and 10% in those of heroine) and the ions $(M-R)_\beta^+$ and $(M-R-2nH)_\beta^+$ with $m/z=146$, 144 with the structure N-methylphenyldihydropiridinium and N-methylphenylpiridinium, respectively; their intensity is 100% and they have the characteristic lines only in the SI mass spectra.

The availability of quasimolecular ions and characteristic of SI opioid ions with $m/z=144$, 146 makes it possible to identify narcotics sufficiently reliably. The high SI selectivity to nitrogen bases proposes the possibility of the SI-MS analysis of mixtures with narcotics and products of their metabolism without preliminary chromatographic separation.

To investigate the analytical possibilities of SI-MS, samples of urine extracts of heroine users were studied by SI. For comparison, the same samples were analyzed by using a HP-6890 chromatograph–EI-MS. Due to the fast metabolisation of opioids in humans establishing the primary structure of the used narcotic is difficult and the analysis is reduced, as a rule, to the detection of the opioid presence in a sample [42]. Heroine in a human is rapidly transformed into monoacetylmorphine that is slowly transformed into morphine and further slightly into normorphine. In illicit heroine acetylcodeine is always present as an impurity.

The SI mass spectra of the urine sample extract of a heroine user is given in Fig. 10d. The mass spectra is sufficiently 'rich' and informative. The baseline is a series with $m/z=144$, 146 characteristic of opioids. The ion lines with $m/z=326$, 324, 284, 282 correspond to the quasimolecular ions $(M-H)^+$ and $(M-3H)^+$ of the products of heroine metabolism in a human organism, respectively, to acetylmorphine and morphine; similarly, the ion lines with $m/z=340$, 338, 298, 296 to acetylcodeine and codeine, and those with $m/z=270$, 284 to normorphine and norcodeine. Thus, the SI mass spectrum of the urine sample consists of a superimposition of the SI mass spectra of the products of illicit heroine metabolism — acetylcodeine, acetylmorphine, codeine, morphine, norcodeine and normorphine.

The comparison of the analytical possibilities of the SI-MS method with GC–EI-MS shows that the sensitivity of SI-MS is essentially higher. The above-indicated sample cannot be identified by the HP-6890 instrument. The preliminary estimations show that the detection limit of opioids and their metabolites by the SI-MS methods is ~ 1 ng/ml that is 100 and more lower than that with the use of EI-MS.

Thus, the high efficiency and selectivity of SI and the characteristic SI mass spectra permit reliable identification of opioids in mixtures without preliminary chromatographic separation of the samples with the sensitivity essentially higher than that of the GC–MS method with electron ionization.

4. Conclusion

The unique selectivity and efficiency of SI of organic nitrogen bases, the special character and predictability of the ions formed by SI are realized in a complex of specific gas-analytical devices beginning from simple diode detectors, SID for GC portable flowing diode SI gas analyzers and indicators of narcotics to SI-IMS and SI-MS. The technical, metrological and operational characteristics of the gas-analytical SI devices are defined. They allow the selective registration and analysis of the trace amounts of nitrogen bases (from amines, degradation products of chemical warfare, herbicides to natural and synthetic narcotics and other abused medicinal preparations) in the air (from $\sim 10^{-10}$ g/l) and in the mixture of compounds (from $\sim 10^{-12}$ g),
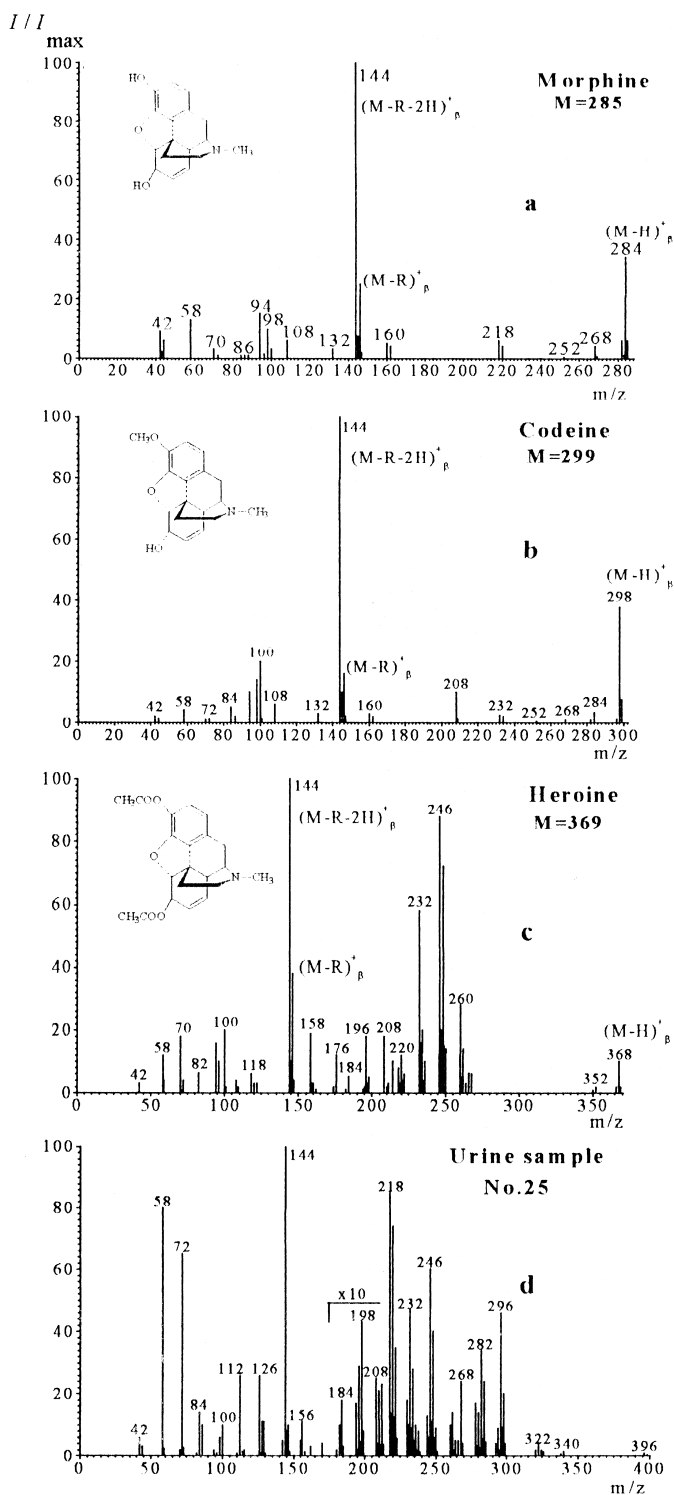
Fig. 10. SI mass spectra of CAS opioids and the urine samples of a heroine user.

often even with no preliminary separation of mixtures.

The SI devices are very simple in design. Their basis is the developed effective and stable emitters from a single crystal of Mo doped by Ir to operate in an air atmosphere and from oxidized W to operate in a vacuum.

The developed SI methods and devices can be, and are used, in the different fields of science and industry, from a selective sensor to monitor environment and ensure sanitary standards at working places where nitrogen bases are produced or used, to the control of hermeticity of objects with large volumes and lengths; from the chromatographic and mass-spectrometric analysis of complex mixtures of amines and their derivatives, to detection and identification of trace amounts of narcotics and other abused drugs in toxicology and criminology. The unique characteristics of the analytical SI devices allow us to hope for essential extension of the fields of their application.

Acknowledgements

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