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Journal of Chromatography A, 704 (1995) 473–482

JOURNAL OF  
CHROMATOGRAPHY A

## Chromatographic determination of trace amounts of amines using a surface ionization detector

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First received 17 May 1994; revised manuscript received 21 October 1994; accepted 14 November 1994

### Abstract

The results of comparative investigations showed the possibility of the chromatographic detection of trace amounts of amines (primary, secondary, tertiary and quaternary) in mixtures using a modified surface ionization detector. The potential (theoretical) characteristics of the surface ionization detector (ionization efficiency, sensitivity, detection limits, linear ranges, etc.) were calculated on the basis of an experimental study of the concentration dependences of the detector signal on the amount of substance under analysis ( $10^{-4}$ – $10^{-9}$  g). The unique sensitivity of the detector with respect to tertiary amines,  $10^{-14}$  g/s, is shown, in addition to the possibility of the selective registration and identification of quaternary ammonium salts.

### 1. Introduction

The wide application of nitrogen-containing bases in various areas of the chemical and chemical–pharmaceutical industries and the necessity to determine trace amounts of physiologically active and carcinogenic substances in complex mixtures have stimulated the development of highly sensitive selective and rapid methods for the determination of amine containing substances [1,2]. Among the methods considered, recording of amines, hydrazines and their derivatives based on the surface ionization (SI) phenomenon is of particular interest [3–5]. Surface ionization consists in the formation of ions during thermal desorption of particles from a solid surface. Positive ions are formed as a result of the isoenergetic tunnel transition of an

electron from a desorbing particle into the solid. The detection of the SI of organic compounds and subsequent systematic mass spectrometric study have revealed the general regularities of the SI of organic compounds of different classes [4–5]. It has been found that as a rule it is not the initially adsorbed molecules that become ionized but the products of their heterogeneous reactions, followed by the formation of particles with relatively small ionization potentials; more often these are the products of dissociation, and rarely of associations with the formation of quasi-molecular particles:  $(M + H)$ ,  $(M - H)$ ,  $(M - R)$ , where  $M$  is a molecule,  $H$  is a hydrogen atom and  $R$  is a radical. Nitrogen-containing organic compounds such as amines, hydrazines and their derivatives appeared to be the most effectively ionizable. The efficiency of the ionization of these substances depends on the nature of the functional group. It increases, for example,

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in the series of primary, secondary and tertiary alkylamines, for the tertiary type reaching values of  $0.1\text{--}0.05\text{ A/Pa}\cdot\text{cm}^2$ . Thus, one ion is formed by every 2–5 adsorbed molecules. Organic compounds of other classes are significantly more weakly ionized and molecules of simple gases appeared to be virtually non-ionizable. This led to the development of a simple selective detector for amines, hydrazines and their derivatives on the basis of SI [6,7].

The first instruments for surface ionization detection (SID) demonstrated unique sensitivity and selectivity of amine registration and good prospects for employment as selective detectors in gas chromatography [7,8]. Later, SID was used in a number of studies [9–11] as an illustration of the possibility of determining trace amounts of series of alkylamines, polyaromatic hydrocarbons, terpenes, steroids and some nitrogen-containing medicinal preparations in complex mixtures [8–10]. However, at present the wide application SID is restricted by the lack of systematic data from investigations of its analytical characteristics. For this reason, this paper presents the results of comparative investigations that show the possibility of detecting chromatographically trace amounts of alkylamines (primary, secondary, tertiary and quaternary) in complex mixtures using SID. The data permit a complete set of unified characteristics of SID to be obtained that will allow specialists to establish the practical problems where this detector could be employed with the highest efficiency.

## 2. Experimental

The results presented here were obtained under the same experimental conditions using a chromatograph (TSVET-500) equipped with an experimental model of a surface ionization detector with an indirect incandescence emitter. The detector was designed specially for chromatographs of this kind [12]; later an analogous detector was connected to other types of chromatographs and the same characteristics were obtained in these experiments. Fig. 1 shows the design and the scheme of the electric circuitry for

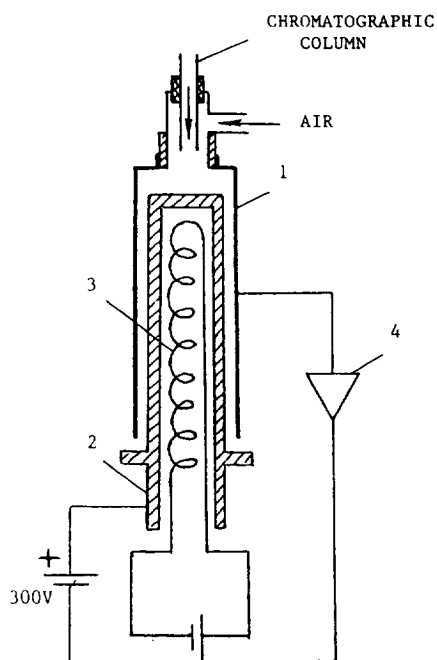


Fig. 1. Design of surface ionization detector with indirect incandescence emitter and the connecting circuitry. 1 = Collector; 2 = Thermoemitter; 3 = Nichrome heater; 4 = charge amplifier.

the detector and indirect incandescence emitter. The detector consists of a two-electrode device containing the thermoemitter (2) in the form of a hollow cylinder and enclosed by cylindrical ion collector (1). The thermoemitter is heated to the operating temperature of  $650\text{--}700\text{ K}$  by a Nichrome heater (3) located in the inner cavity of the thermoemitter. To provide effective collection of ions desorbing from the thermoemitter, a potential difference ( $300\text{ V}$ ) is applied between the thermoemitter and the collector. Provided that stability of the emission and catalytic characteristics of the thermoemitter obtain, the ion current recorded by the electrometer (4) is proportional to the number of molecules of analyte amines adsorbing on the thermoemitter and, hence, proportional to the concentration of ionizing molecules in the mixture.

The detector with an indirect incandescence emitter has the following advantages over detectors with direct incandescence wire thermoemitters used previously [7,9]: owing to the high heat

conductivity of the massive thermoemitter, rectangular distribution of temperature all over its operating length (38 mm) is provided; the noise immunity increases owing to complete isolation of the incandescence circuit and the circuit of ion current measurements; and the thermoemitter operating period rises considerably and the degree of influence of outside factors (temperature variations, flow velocity of the mixture under analysis through the detector, vibrations, etc.) on the detector characteristics decreases.

The material from which the thermoemitter is constructed influences the main characteristics of the detector. The operating surface of the thermoemitter should have a maximum work function and maintain constant emission and catalytic properties with prolonged heating in gas–air mixtures (air or inert gas) containing organic compound vapours. Oxidized refractory metals are known to meet these requirements, primarily molybdenum [13] and some other metals (e.g., Ir, Re, Pt) [10], when oxygen or air is passed continuously through the detector. In addition, very rigid requirements are placed on the purity of the material, as there should be no impurities of elements with small ionization potentials, e.g., alkali metals. On heating the thermoemitter their atoms diffuse from the bulk to the surface and evaporate from it as ions that generate considerable background currents. To purify them from admixtures, the thermoemitters produced must be subjected to prolonged vacuum annealing at  $>2000$  K. We have found a continuous decrease with time (during a year of operation) in the ionization efficiency of thermoemitters made from polycrystalline molybdenum. A brown coating was formed on the operating external surface of such emitters, and appeared not only on thermoemitters operated with organic vapours but also on control thermoemitters intended for registering background currents only. This indicates that surface degradation is the result of diffusion from the bulk of hardly evaporating elements. It is likely that these are compounds of chromium evaporating into the inner cavity of the thermoemitter from the Nichrome heater. To prevent such degradation, it has been recommended to use single-crystal

molybdenum as the initial material [14]. The diffusion rate of foreign atoms through the single-crystal lattice is an order of magnitude less than that over grain boundaries of polycrystalline molybdenum, so even at the same purity of the initial materials the degree of long-term degradation of the single-crystal surface by diffusion flow from the bulk is essentially less than that of polycrystals.

In our experiments the chromatograms were recorded simultaneously using two types of detection, namely surface ionization detection (SID) and conventional flame ionization detection (FID), the detector being connected in parallel to the outlet of the chromatograph column. The carrier gas flow on the outlet of the column was divided in the ratio SID:FID = 1:3. This arrangement allowed not only the ratio of detector signals,  $I_{\text{SID}}/I_{\text{FID}}$ , to be obtained with high accuracy, which was necessary for functional group analysis of amines (as was shown previously [15]), but also permitted the sample dose ( $m$ ) entering the evaporator to be controlled independently by the signal of each detector. Moreover, the constancy of the  $I_{\text{SID}}/I_{\text{FID}}$  ratio with changes in the amount of sample entering the evaporator indicated that the characteristics of each detector remained constant during comparative analyses. After careful training of the thermoemitter and special steps for purification of the carrier gas and air, the background current did not exceed  $10^{-10}$  A with a noise level of  $10^{-13}$  A.

### 2.1. Procedure

Comparative analyses of the efficiency of amine ionization were performed using solutions in which standards of alkylamines of various classes were used: primary = hexylamine (HEA), allylamine (ALA) and *n*-butylamine (BA); secondary = diethylamine (DEA), diisobutylamine (DiBA), diisopentylamine (DiPA) and dipentylamine (DPA); tertiary = triethylamine (TEA), tributylamine (TBA), tripropylamine (TPA) and dipropylpropargylamine (DPPA). The following simplest structures were used as representatives of quaternary amines: tetraethylam-

monium chloride, tetraethylammonium bromide and acetylcholine (ACH), the last being more complex in structure.

For all substances under analysis, the SID characteristics were determined by the procedure of calibrated insertion of a sample into the detector [16]. As a rule, the dependences of the charge in coulombs,  $Q = \int i(t) dt$ , obtained in SID on the dose of the substance under analysis inserted into the chromatograph evaporator were monitored. Toward this end, six calibration solutions were prepared by successive dilution with concentrations  $C = 10, 1, 10^{-1}, 10^{-2}, 10^{-3}$  and  $10^{-4}\%$  (v/v). Samples with volume  $V = 5$  ml were injected into the evaporator of the chromatograph with a microsyringe and they contained  $m = V\rho C/100$  g of the substance under analysis (where  $\rho$  is the specific gravity of the component under analysis), which corresponded to the amine doses from  $10^{-4}$  up to  $10^{-9}$  g. In check experiments with a solution of tributylamine in acetone, a wider dose range was used (from  $10^{-12}$  up to  $10^{-4}$  g). However, in this instance the requirements on the conditions for preparing and carrying out the analysis (purity of carrier gas, preparation of samples and injection into the evaporator) became more rigid. At the same time, the relative error in the doses increased significantly. Therefore, subsequently the dose range in all experiments was limited to  $10^{-9}$ – $10^{-4}$  g.

A separate syringe was used for each kind of amine and when using different concentrations the syringe was washed thoroughly in the solvent. Each time the experiment began with the use of the solution with the minimum amine concentration.

Acetone, hexadecane and sometimes distilled water and ethanol were used as solvents for the amines. Before the preparation of the solutions a chromatogram of the solvent was first taken.

Glass columns (200 cm  $\times$  3 mm I.D.) were used for chromatographic separation. Depending on the substance–solvent pair, various sorbents were used: non-polar 4% Apiezon (Ap) + 1% KOH on Chromatone G and polar 0.5%  $\text{Na}_3\text{PO}_4$  + 5% PEG-1000 on Chromosorb G AW [17].

All experiments were carried out within the same temperature regime: thermostated columns, 100°C; evaporation cell, 140°C; and thermoemitter, 660 K. Helium was used as the carrier gas with a flow-rate of 30 ml/min. The flow-rate of air necessary to stabilize the characteristics of the operating surface of the thermoemitter was 100 ml/min.

Quaternary salts (QAS) were dissolved in ethanol or distilled water, in view of the practical problems of their determination in biological liquids.

SID characteristics were calculated using plots of the dependences  $Q = f(m)$  in the following way:

(i) ionization efficiency (according to Lovelock):

$$E = \frac{MQ}{meN_a}$$

where  $M$  is the relative molecular mass and  $N_a$  is Avogadro's number;

(ii) sensitivity ( $K$ ):

$$K = \frac{Q}{m} \text{ (C/g)}$$

(iii) detection limit:

$$m_{\min} = -\frac{Q_{\min}}{K} = \frac{2 \int i_n dt}{K} \text{ (g/s)}$$

where  $i_n$  is the level of noise;

(iv) linear dynamic range (LDR):

$$\text{LDR} = m_{\max}/m_{\min}$$

where  $m_{\max}$  is the amount of substance under analysis at which deviation from linearity of the  $Q = f(m)$  dependence begins;

(v) selectivity ( $S$ ):

$$S = \frac{K_1}{K_2}$$

where  $K_1$  is the sensitivity of SID relative to the amines under analysis and  $K_2$  is the sensitivity of SID relative to the substance with respect to which the selectivity is estimated;

(vi) the coefficient of relative sensitivity,  $I_{\text{SID}}$ /

$I_{\text{FID}}$ , i.e., the ratio of the SID and FID signals with parallel registration; and

(vii) reproducibility of the results, which characterizes the similarity of the results of repeated measurements performed under the same conditions.

### 3. Results and discussion

#### 3.1. Determination of primary, secondary and tertiary amines

Fig. 2 (lines 1–11) shows the results of the chromatographic determination of the dependences of the amount of the charge registered in SID on the dose of various kinds of amines inserted

into the evaporator. It can be seen that all dependences have the same slope. Deviation from linearity for all substances begins when the charge  $Q \sim 10^{-5}$  C is collected from the thermo-emitter, which corresponds to a current density  $j = 5.1 \cdot 10^{-6}$  A/cm<sup>2</sup>. Depending on the functional group of the amines, their plots are arranged at various levels corresponding to various sensitivities  $K$  (C/g). The first part with  $K > 1$  includes the plots corresponding to all tertiary amines, the second part (dashed region) with  $10^{-2} < K < 1$  contains all plots of secondary amines and the third part with  $K < 10^{-2}$  contains all plots of primary amines. The main SID characteristics calculated relative to various kinds of amines are given in Table 1. It is seen that the ionization efficiency  $E$  of SID for ter-

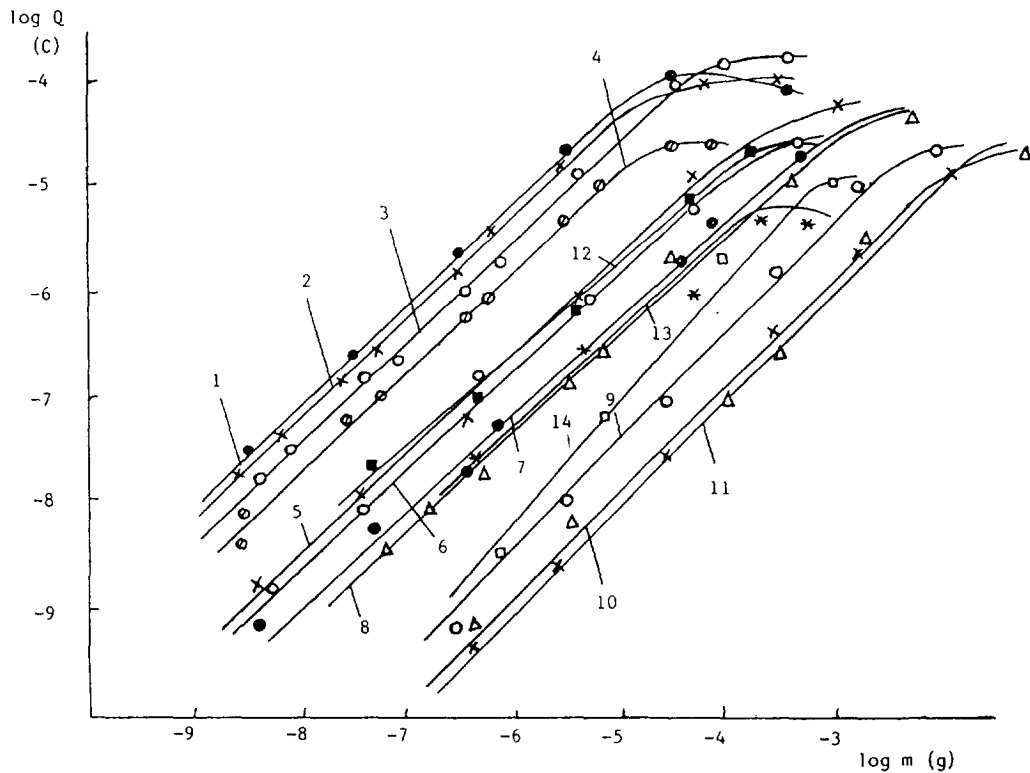


Fig. 2. Plots of the dependences of SID output signals on the amount of substance introduced. Tertiary amines: 1 = dipropylpropargylamine (DPPA); 2 = tripropylamine (TPA); 3 = tributylamine (TBA); 4 = triethylamine (TEA). Secondary amines: 5 = dipentylamine (DPA); 6 = diisopentylamine (DiPA); 7 = diisobutylamine (DiBA); 8 = diethylamine (DEA). Primary amines: 9 = hexylamine (HEA); 10 = alkylamine (ALA); 11 = *n*-butylamine (BA). Quaternary amines: 12 = tetraethylammonium chloride; 13 = tetraethylammonium bromide; 14 = acetylcholine.

Table 1  
 Characteristics of the surface ionization detector

Amine	Ionization efficiency, $E_i$	Sensitivity, $K$ (C/g)	Detection limit (g/s)	Linear dynamic range (LDR)	Selectivity (relative to ketone hydrocarbons), $S_k$	$I_{SID}/I_{FID}$	Reproducibility (%)
<i>Tertiary</i>							
DPPA	$1.3 \cdot 10^{-1}$	7.2	$2.7 \cdot 10^{-14}$			10000	
TPA	$1.8 \cdot 10^{-1}$	6.0	$3.3 \cdot 10^{-14}$			8000	3-4
TBA	$1.6 \cdot 10^{-2}$	3.0	$6.6 \cdot 10^{-14}$	$10^8$	$10^6 - 10^8$	6000	
TEA	$2.0 \cdot 10^{-2}$	2.1	$9.0 \cdot 10^{-14}$			4000	
<i>Secondary</i>							
DPA	$2.5 \cdot 10^{-2}$	$2.9 \cdot 10^{-1}$	$3.4 \cdot 10^{-13}$			100	
DiPA	$1.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$7.0 \cdot 10^{-13}$	$10^6$	$10^6 - 10^5$	488	<5
DiBA	$2.8 \cdot 10^{-3}$	$3.3 \cdot 10^{-2}$	$3.0 \cdot 10^{-12}$			80	
DEA	$1.4 \cdot 10^{-3}$	$3.0 \cdot 10^{-2}$	$3.3 \cdot 10^{-12}$			90	
<i>Primary</i>							
HEA	$8.0 \cdot 10^{-5}$	$2.8 \cdot 10^{-3}$	$3.4 \cdot 10^{-11}$			30	
ALA	$2.5 \cdot 10^{-5}$	$1.4 \cdot 10^{-3}$	$1.0 \cdot 10^{-10}$	$10^5$	$10^4$	5	<5
BA	$3.5 \cdot 10^{-5}$	$3.5 \cdot 10^{-4}$	$2.8 \cdot 10^{-10}$			70	
<i>Quaternary</i>							
Tetraethylammonium chloride	$2.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-1}$	$1.0 \cdot 10^{-13}$	$10^6$		3000	5-6
Tetraethylammonium bromide	$4.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-1}$	$1.0 \cdot 10^{-13}$	$10^6$	$10^6 - 10^5$	4000	5-6
ACH	$2.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-11}$	$10^5$		2000	5-6

tertiary amines is  $10^{-1}$ – $10^{-2}$ . This value is defined by Lovelock as the ratio of ion flows,  $\nu_k^+$ , of all recorded kinds of ions to the total flow,  $\nu$ , of ionizing molecules directed to the detector inlet. By introducing  $\nu_{\text{mol}}$  (the fraction of molecules from the flow  $\nu$  that is incident on the thermoemitter surface) into this ratio one can obtain [7]

$$E = \frac{\sum_k \nu_k^+}{\nu} = \frac{\sum_k \nu_k^+}{\nu_{\text{mol}}} \cdot \frac{\nu_{\text{mol}}}{\nu} = \beta_{\text{mol}} \cdot \xi$$

where  $\beta_{\text{mol}} = \nu_k^+ / \nu_{\text{mol}}$  is an integral coefficient of the surface ionization detector defined by the thermoemission and catalytic properties of thermoemitter material;  $\xi$  is a factor characterizing the perfection of the detector design as it defines the coefficient of utilization of a substance.

Using mass spectrometric data,  $\beta_{\text{mol}}$  was calculated for tertiary amines to be 0.2–0.1 [3,4,17]. Hence, the coefficient of utilization of a substance for a given design of the detector is close to the maximum value. The limit of detection of tertiary amines is  $m_{\text{min}} = 10^{-14}$  g/s, which exceeds considerably those with the best models of flame ionization [18] and thermoionic detectors [19]. One can obtain analogous sensitivity using an electron-capture detector, but then the preliminary conversion of amines into halogen-containing compounds is necessary, which makes the analysis complex [20]. It should be noted that limits of detection and the linear dynamic ranges (LDR) given in Table 1 are of a relative character as they were calculated on the assumption that the linearity of all plots that applies in the small-dose region is maintained up to the double noise of  $2I_n = 2 \cdot 10^{-13}$  A, but this requires experimental confirmation. As we pointed out, such attempts have been made and at best reproducible results and linearity were obtained only for doses of  $10^{-11}$  g. The high sensitivity of SID is confirmed by the ratio of the SID and FID signals: for tertiary amines it equals  $10^3$  with an error of 5%, for secondary amines  $10^2$  with an error of 10% and for primary amines less than  $10^2$  but with an error of 25%. As is known, the different sensitivities relative to amine subclasses may be used for functional group analysis [15].

The unique selectivity of SID towards nitrogen-containing bases is known from direct mass spectrometric investigations surface ionization [5]. The chromatogram in Fig. 3 illustrates this effect, from which it is seen that the values of the recorded peaks for acetone and for TBA are almost the same, although the amount of TBA introduced ( $3.1 \cdot 10^{-9}$  g) is  $6.2 \cdot 10^6$  times less than that of acetone ( $1.58 \cdot 10^{-3}$  g). When using samples containing amines and saturated hydrocarbons as solvent only one amine peak was registered for such concentrations.

The reproducibility of the analytical results obtained by SID is determined by the SID operating conditions and by the thermoemitter state. This could be revealed during operation with simultaneous SID and FID. When a solvent and the ionizing component are very different from each other, then the reproducibilities of the results for both detectors correlate independently of the kind of solvent and are within the range 5–6%. However, if the retention time of an amine is close to that of the solvent, then with non-selective FID the main peak of the solvent overlaps the peak of the dissolved component under analysis. In this event owing to its high selectivity, only one amine peak is registered by SID, but the reproducibility of the results becomes worse owing to oversaturation of the thermoemitter by the solvent vapours. Hexadecane proved to be the most convenient solvent. When using columns packed with Apiezon sorbent (4% Ap + 1% KOH), the retention time of amines is of the order of minutes whereas that of the solvent is up to 8 h, so the continuous

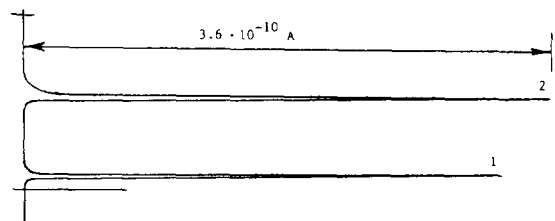


Fig. 3. Chromatogram of a mixture ( $2 \cdot 10^{-3}$  cm<sup>3</sup>) containing  $2 \cdot 10^{-4}\%$  (v/v) of tributylamine in acetone: 1 = acetone (retention time  $t_r = 15$  s); 2 = tributylamine ( $t_r = 180$  s). The ion current was registered on the same scale of the charge amplifier.

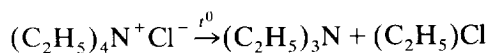
analysis of amines may be carried out using both detectors during the whole operating time, as has been recommended [21].

### 3.2. Determination of quaternary amines

The results of the chromatographic determination of the dependence of the amount of charge registered in SID on the dose of quaternary ammonium salts (QAS) inserted into the chromatographic evaporator, namely tetraethylammonium chloride  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^-$ , tetraethylammonium bromide,  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Br}^-$ , and a typical representative of a mediator of natural origin, acetylcholine chloride,  $\text{CH}_3\text{COOCH}_2\text{-CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ , are presented in Fig. 2 (plots 12–14). Such dependences were obtained irrespective of the kind of solvent employed, distilled water or ethanol. The results of calculations of the SID characteristics relative to QAS are given in Table 1.

Fig. 4 shows typical chromatograms for comparison that were registered using SID and FID simultaneously under various conditions of analysis with the same dose  $m = 2 \cdot 10^{-5}$  g of triethylamine and tetraethylammonium chloride. One can see that the high selectivity of SID allows amines to be reliably registered irrespective of the conditions of the chromatographic separation of the solvent and amine under analysis, whereas for the analysis with non-selective FID it is necessary to achieve the effective chromatographic separation of the amines and solvent. The sensitivity  $K$  of SID when registering QAS is in the range 0.01–1 C/g, which corresponds to the sensitivity of secondary amines, and the ratio of signals  $I_{\text{SID}}/I_{\text{FID}} = 4000$  corresponds to tertiary amines. Moreover, the times of sample retention in the column when inserting both tetraethylammonium chloride and bromide into the chromatographic evaporator are the same and coincide with the retention time of triethylamine.

Having analysed these data, the following conclusion could be drawn: QAS decompose in the chromatographic evaporator into tertiary amines, e.g., in accordance with Hoffman degradation:



(where  $t^0$  denotes thermal heating) and the products of this reaction then are subjected to chromatographic separation, which is in accordance with the generalized conclusions concerning the chromatography of quaternary amines presented in detail by Anderson [18].

To locate where QAS are transformed into tertiary amines, experiments were carried out with various temperatures of the evaporator and a constant temperature of the column.

Fig. 5 shows the alteration of the peak shape registered during the injection of  $10^{-5}$  g of acetylcholine at a constant column temperature  $T_c = 150^\circ\text{C}$  for different temperatures of the evaporator ( $T_{\text{ev}}$ ). One can see that the peak at  $T_{\text{ev}} = 180^\circ\text{C}$  has a diffuse shape that could be explained by the low rate of transformation of acetylcholine into tertiary amine. With the increase in  $T_{\text{ev}}$  the rate of the transformation reaction in the evaporator increases. This process affects the peak width, making it more symmetric. At  $T_{\text{ev}} > 260^\circ\text{C}$ , the peak width becomes independent of  $T_{\text{ev}}$ , but it is anyway slightly wider than that of the peak registered for the injection of the corresponding tertiary amine (Fig. 4a–d).

In analogous experiments with triethylamine, the peak shape appeared to be independent of  $T_{\text{ev}}$  as low as  $120^\circ\text{C}$ . This evidence indicates that decomposition of QAS into tertiary amines takes place mainly in the evaporation cell. Nevertheless, even at high  $T_{\text{ev}}$ , a certain fraction of QAS enters the chromatographic column where they may also be transformed into tertiary amines. This results in specific differences in the shape of the chromatographic peak of QAS from that of the corresponding tertiary amine. The latter may be used for the determination of QAS in complex mixtures by the analysis of data including the retention times and the shapes of the peaks recorded.

## 4. Conclusions

Systematic studies have been made of the main characteristics of a modification of the



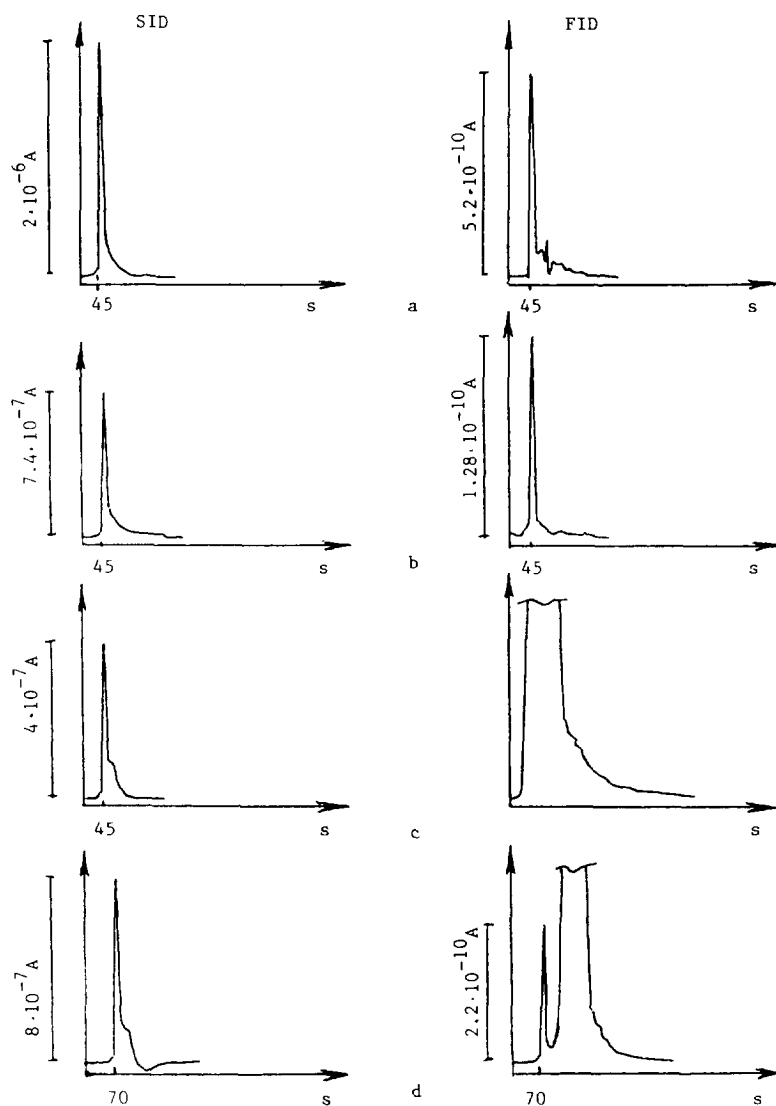


Fig. 4. Comparison of chromatograms obtained for injection of (a, b) aqueous and (c, d) alcoholic solutions of (a) triethylamine and (b–d) solutions of tetraethylammonium chloride using the columns with various sorbents: (a–c) Apiezon with potassium hydroxide and (d) PEG-1000.

surface ionization detector with an indirect incandescence emitter. The values of the characteristics obtained confirm the excellent sensitivity and selectivity of nitrogen-containing bases registered by the surface ionization method. By using SID the functional group analysis of trace amounts of amines in various mixtures can be carried out. The highest sensitivity was obtained

relative to tertiary amines and the detection limit is ca.  $10^{-14}$  g/s.

The present detector may be used for the selective registration and identification of quaternary amines. The detection limit of QAS in solutions is ca.  $10^{-13}$  g/s.

The high sensitivity and selectivity of SID relative to nitrogen-containing bases suggest the

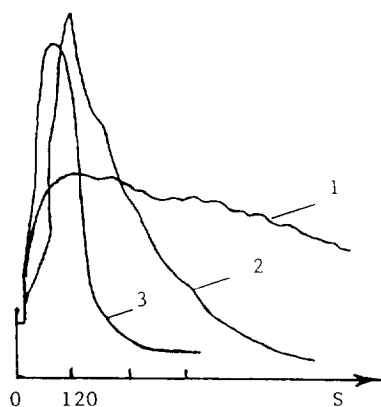


Fig. 5. Alteration of peak shape registered on injection of the acetylcholine obtained with constant temperature of the chromatographic column (150°C) and different temperatures of the evaporator:  $T_{ev}$  = (1) 180, (2) 220 and (3) 260°C.

development of improved methods for the detection and identification of various amines and their derivatives.

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