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CERTAIN ASPECTS OF THE THEORY AND THE PROSPECTS FOR THE DEVELOPMENT OF IONIZATION CHROMATOGRAPHIC DETECTION AND IDENTIFICATION OF SUBSTANCES

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SUMMARY

Regularities of detection based on the Penning effect in neon have been examined. Detection in the saturation current mode is shown to be accompanied by anomalous weakening of the Penning effect by substances with relatively high ionization potentials such as hydrogen, argon, nitrogen and sulphur dioxide. It has been established that this phenomenon is observed in high-purity neon when it is contaminated by substances with relatively high ionization potentials such as organic compounds and moisture. The phenomenon observed is explained on the basis of the concept of the essential role of excimeric molecules in the Penning effect and the processes of their quenching as a result of collisions with the molecules of some substances to be detected.

The regularities found have been used in new methods for the quantitative interpretation of chromatograms and the identification of inorganic substances. These methods were applied in the chromatographic analysis of the atmosphere of Venus on the Soviet interplanetary stations Venus 11, 12, 13 and 14.

Aspects of identifying organic substances, based on the regularities of flame ionization detection, have been examined. It has been shown to be possible to use the dependence of the detection ionization efficiency on the composition and structure of the molecules of organic substances for the identification of classes of compounds and individual substances.

INTRODUCTION

General-purpose ionization methods of detection, to which methods based on the Penning effect (using helium and neon) and flame ionization methods belong, are usually regarded from the point of view of obtaining quantitative information on the chromatographic determination of impurities. At the same time, the diversity of the elementary processes that determine the signals of radio- and flame ionization detectors results in certain detection regularities that carry information on the physical characteristics of the components to be determined, including that on the composition of compounds and their structure.

Helium and neon detectors can be regarded as completely universal, whereas

the flame ionization detector is universal for organic compounds. This is why the use of the regularities of these detection methods for the identification of substances, together with obtaining quantitative data on their contents, appears to be of great advantage. This was one of the objectives of the present work.

The second objective was to find new methods for the quantitative interpretation of chromatograms as applied to those instances when the real characteristic of a detector in an experiment cannot be determined in advance. Such a situation arises when a radioionization detector is used in outer-space experiments, *e.g.*, in the chromatographic analyses of the atmospheres of solar system planets. In these instances the specific characteristics of detectors, including the sensitivity, linear dynamic range or non-linear charachteristics of transformation obtained on Earth, often cannot be preserved throughout the flight of the apparatus to the planet, and the possibilities of their being comprehensively checked directly before performing the chromatographic analysis are very limited.

As applied to the neon method of detection, both of the above-mentioned objectives were achieved in connection with the use of this method in the chromatographic analysis of the atmosphere of Venus on the Soviet interplanetary stations Venus 11 and 12 (1978) and Venus 13 and 14 (1982)[1–4]. A detailed study of one of the detection methods based on the Penning effect was necessary in this instance because the classical concepts of the Penning effect, and the analyses of helium, neon and argon using detection methods based on them, performed by Lovelock[5], Knapp and Meyer[6], Rotin[7] and other investigators, failed to describe fully or even explain the observed characteristics of detectors.

EXPERIMENTAL

The experimental study of ionization detectors was performed on chromatographic devices based on general-purpose gas chromatographs. The dosing of liquids was accomplished with a 1-μl microsyringe and the dosing of gases with a crane-type dosing apparatus with a constant macrodose or a special dosage calibrator with eight doses whose volume varied in approximately geometric progression from 0.5 to 32 μl.

Low-boiling gases were, as a rule, separated on columns of 5 Å molecular sieves and organic substances, water and sulphides on columns of Polysorb 1, when necessary modified with polyethylene glycol adipate.

The power was supplied to the detectors at a constant voltage. The measuring circuit of the detectors made it possible to record chromatograms and to measure the background and useful signals of the detector in units of current.

Whenever necessary the carrier gas purity was varied either by additional cryogenic purification of high-purity gases or by contaminating them with the vapours of liquid substances fed to the detector inlet by Desty *et al.*'s method[8]. The carrier-gas pressure in the detector could be adjusted by means of a special pressure stabilizer within the range 1–4 atm.

Some of the experiments were conducted directly on Sigma and Sigma-2 instruments designed for investigating the Venus atmosphere[2,3].

RESULTS AND DISCUSSION

Detection in pure neon. Saturation current mode

In the saturation current mode the rate of metastable atom formation depends neither on the electric field nor on the concentration of impurities and is determined only by the interaction of radioactive radiation with the carrier gas atoms. Detection based on the Penning effect in the saturation current mode is, therefore, an independent and stable version of the helium and neon detection methods.

For detectors with inter-electrode distances of 1 and 4 mm, equipped with tritium–titanium β-sources, the relationships between the peak height and the sample volume were obtained for dosages of mixtures containing argon (5.0%), nitrogen (5.0%), krypton (2.8%), methane (10.0%) and xenon (3.12%). The volume of the samples varied from $5 \cdot 10^{-4}$ and $3.2 \cdot 10^{-2}$ cm^3. The experiments were conducted in the pressure range 1–4 atm. High-purity neon carrier gas was additionally purified with 5 Å molecular sieves at the temperature of liquid nitrogen. The separation conditions were chosen in such a way that the signal could be observed not only in the linear region but also at the approach to saturation.

The dependence of the detector signal, I_c, on the concentration C of a sample substance is satisfactorily described by the equation[6,7]

$$I_c = I_{\text{met max}} \cdot \frac{C}{\dfrac{k_d}{k_i} + C} \tag{1}$$

where $I_{\text{met max}}$ is the maximum detector signal resulting from the complete expenditure of the carrier gas metastable atoms on ionization in the Penning reaction and k_d and k_i are the rate constants of metastable atoms deactivation and impurity ionization.

Fig. 1 shows as an example the experimental data obtained at $P = 1$ atm. From eqn. 1 there follows directly a linear dependence of I/I_c on I/C. Therefore, in a chromatographic experiment with a variable sample volume there must be a linear
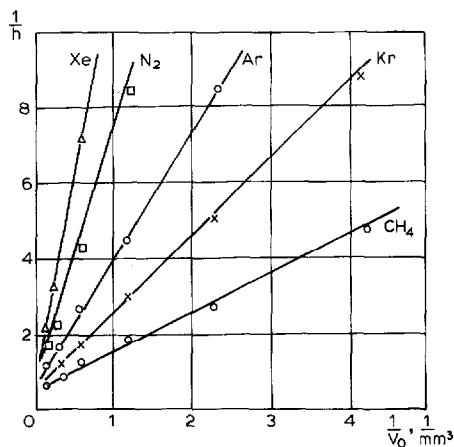

Fig. 1. Neon detector signal for different substances *vs.* sample volume. $P = 1$ atm; $l = 1$ mm.
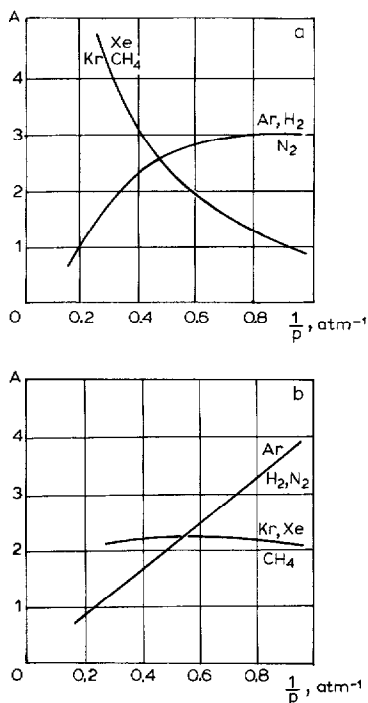
Fig. 2. Neon detector sensitivity to different substances *vs.* gas pressure. (a) $l = 1$ mm; (b) $l = 4$ mm.

dependence between the inverse of the peak height (h) and the sample volume (V_0). In our case the deviation from the linear h *vs.* V_0 dependences did not exceed 2%. Eqn. 1 can therefore be used to plot detector calibration characteristics.

The classical concepts of the Penning effect from which eqn. 1 was obtained do not explain, however, all the regularities of detection. This is primarily true for the dependence of the detector signal on gas pressure.

Fig. 2 shows the dependences of the neon detector sensitivity to different substances on the gas pressure in the chamber. The course of these dependences for detectors with 1 and 4 mm inter-electrode distances should be different because the conditions of the absorption of tritium radiation β-particles is different in these instances: the mean path of β-particles in neon under normal conditions is 3 mm. However, the different course of the dependences under the same experimental conditions for different substances requires a special explanation.

A similar regularity was observed by Jesse and Sadauskis[9] when they studied the Penning effect in helium. They noted that substances characterized by a different dependence of the rate of the Penning reaction on the gas pressure are grouped according to their ionization potentials. They concluded that not only metastable atoms but also metastable molecules of rare gases can take part in the Penning effect.

We shall show below that the participation of metastable (excimeric) neon molecules is responsible for the appearance of a new phenomenon: the anomalous weakening of the Penning effect. This is manifested in neon detection as detection anomalies near the detection limit of the concentrations of substances being analysed.

Anomalous weakening of the Penning effect in the neon detector

When the Sigma chromatograph was prepared for the experiment and the Venus atmosphere was analysed on the Soviet automatic stations Venus 11 and 12 in 1978, we observed for the first time inversion of the neon detector signal in the near-threshold region of the concentrations of certain substances (argon, nitrogen, hydrogen)[1,2]. Later a similar regularity was observed[10] when working with a helium detector in the ionization amplification mode. We noted that in detecting these substances a negative signal was observed in those instances when the initially pure neon was contaminated with compounds whose ionization potentials were lower than those of the substances in question. At the same time, the addition of argon, nitrogen or hydrogen, whose ionization potentials exceed 15 V, to the carrier gas eliminated the anomalous phenomena.

The ascertained regularities can be explained from the concept of the essential role played by long-living excimeric molecules in the processes that determine the Penning effect in neon.

The formation and behaviour of inert gas excimeric molecules have been studied in sufficient detail in connection with the problem of excimeric lasers[11]. Therefore, it appears possible to ascertain their role in ionization processes determining the detection of impurities[11,12]. The rate of formation of helium and neon excimeric molecules under normal conditions is commensurate with the rate of deactivation of metastable atoms of these gases, with no less than half the excited atoms passing through the molecular state.
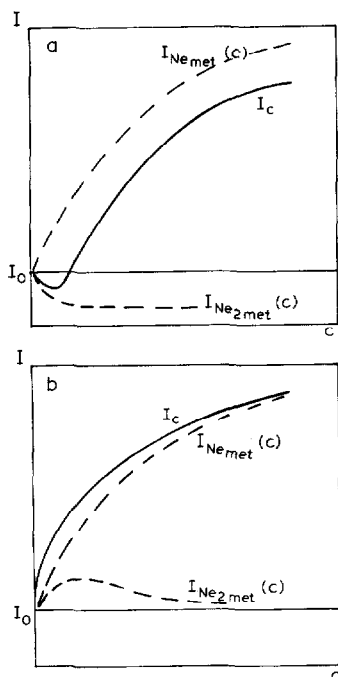

Fig. 3. Determination of the form of the dependences of the neon detector signal on the concentration of (a) substances not ionized by neon excimeric molecules and (b) those ionized by them.

From the point of view of energetics, excimeric molecules have fewer possibilities than the corresponding metastable atoms. The energy released in the collision of an excimer with a molecule is smaller than the metastable atom energy by, first, the value of the chemical bond energy [0.6 eV for Ne_2 $(a^3\Sigma_u^+)$ and 2 eV for He $(a^3\Sigma_u^+)$[12]], and, second, the value of the repulsion energy of unstable Ne_2 and He_2 atoms formed as a result of the excitation energy transfer. The value of this quantity is *ca.* 1–2 eV. As noted by Jesse and Sadauskis[9], there may not be sufficient energy of metastable (excimeric) molecules for the ionization of substances with high ionization potentials (Ar, N_2, H_2, etc.).

An important question is the lifetime of excimeric molecules. In heavy-current discharges the molecules existing in long-lived triplet states are actively converted into short-lived singlet states under the influence of electron collisions. In a non-self-maintained discharge, because of a low concentration of electrons, this process is only slightly effective and, therefore, one can expect the long-lived excimers to play an essential role in the mechanism of the Penning effect.

On the basis of the above discussion, a sufficiently comprehensive nomenclature of elementary processes in a neon detector operating in the saturation current mode can be presented as follows:

Processes (reactions)	Rate constants	
$Ne + e_\beta \rightarrow Ne^+ + e + e_\beta$	v_i	(1)
$Ne + e_\beta \rightarrow Ne_{met} + e_\beta$	v_{met}	(2)
$Ne_{met} + 2Ne \rightarrow 3Ne$	K_{do}	(3)
$Ne_{met} + 2Ne \rightarrow Ne_{2\ met} + Ne$	K_{met}	(4)
$Ne_{2\ met} + Ne \rightarrow 3Ne$	K'_{do}	(5)
$Ne_{met} + M_1 \rightarrow Ne + M^+ + e$	K_{i1}	(6)
$Ne_{2\ met} + M_1 \rightarrow 2Ne + M_1^+ + e$	K'_{i1}	(7)
$Ne_{met} + M_2 \rightarrow Ne + M_2^+ + e$	K_{i2}	(8)
$Ne_{2\ met} + M_2 \rightarrow 2Ne + M_2^+ + e$	K'_{i2}	(9)
$Ne_{2\ met} + M_1 \rightarrow 2Ne + M_1 (+ hv)$	K'_{d1}	(10)
$Ne_{2\ met} + M_2 \rightarrow 2Ne + M_2 (+ hv)$	K'_{d2}	(11)

The detector signal caused by the processes of ionization with neon metastable atoms and excimeric molecules:

$$i_c = ev_{i\ met} \tag{2}$$

is determined from a set of kinetic equations containing the equations of the balance of neon metastable atoms and excimeric molecules, and also the equations for the frequency of ionizing collisions:

$$v_{i\ met} = \sum_{1,2} K_{i\ 1,2} [Ne_{met}] [M_{1,2}] + \sum_{1,2} K'_{i\ 1,2} [Ne_{2\ met}] [M_{1,2}] \tag{3}$$

A simple, although cumbersome, analysis shows that the dependence of the detector signal on the concentration of constant impurity, C_1, of the analysed sample C_2 and gas pressure P can be expressed as an algebraic sum of two functions:

$$I_c = I_{Ne\ met} (C_1, C_2, P) + I_{Ne_2\ met} (C_1, C_2, P) \tag{4}$$

The first term accounts for the processes with Ne_{met} and the second with $Ne_{2\ met}$.

Fig. 3 shows the graphical solution of a set of kinetic equations for two kinds of sample substances: (a) not ionized and (b) ionized by neon excimeric molecules. In the first instance I_{Ne_2met} is always negative, as the sample substance only deactivates $Ne_{2\ met}$ in accordance with reaction 10 and decreases, because of it, the background current partially resulting from reaction 7. In this instance it is obviously necessary for the constantly present impurity to have a low ionization potential.

The regularities noted can result in anomalous weakening of the Penning effect in neon with an impurity component, manifesting itself as negative peaks in the range near the detection limit.

The $I_{Ne\ met}(C)$ and $I_{Ne_2\ met}(C)$ values depend differently on the gas pressure:

$$I_{Ne\ met}(C) \approx \frac{\nu_{met}}{P} \tag{5}$$

$$I_{Ne_2\ met}(C) \approx \nu_{met}\ P^0 \tag{6}$$

The dependence of the detector sensitivity towards certain substances on the carrier gas pressure in the detector can thus indicate which particles are ionizing these substances —metastable atoms of excimeric molecules.

As the anomalous phenomenon of detection is associated with the degree of carrier gas contamination, it can be used to determine the contamination level and, in some instances, also the nature of the contaminating component. For this it is necessary to reproduce the conditions under which the ratios of anomalous peaks to the maximum detector signal for one or several components correspond to the values observed in a certain experiment.

This problem had to be solved in the quantitative interpretation of the chromatograms of the Venus atmosphere[1,2]. The neon detector recorded anomalous signals for nitrogen and argon–oxygen mixture. The modelling of the conditions of the outer-space experiment showed the gas communications of the Sigma chromatograph to be moistened. It is in this event that one can observe anomalous signals of nitrogen and argon in the ratios that were actually observed in the chromatograms of the Venus atmosphere[1-4].

The anomalous signal at the position of the argon + oxygen sum made it possible to identify argon. Reproduction of the moisture level in the analytical system made it possible to determine the real calibration characteristics of the Sigma chromatograph during the experiment on Venus.

Identification of organic substances based on the regularities of flame ionization detection

The ionization efficiency in the flame ionization detection of the molecules of organic compounds is known to constitute an additive function of ionization efficiencies of detecting the groups of atoms making up the molecule, each group being bonded with one carbon atom. The relative ionization efficiency of such groups of atoms is usually characterized by the effective carbon number[13].

The effective carbon number, calculated per carbon atom, for hydrocarbon molecules is close to unity. The carbon atom bonded with oxygen in a molecule of
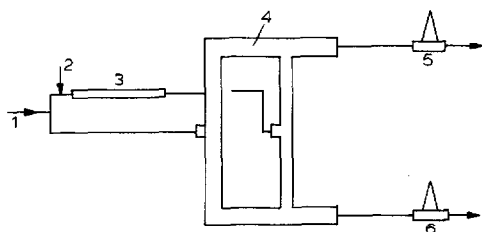
Fig. 4. Schematic diagram of identification device. 1 = Carrier gas inlet; 2 = sample insertion; 3 = separation column; 4 = gas balance; 5 and 6 = flame ionization detectors.

a primary alcohol has a carbon number close to 0.5. In an ether molecule both the carbon atoms bonded with oxygen each have a carbon number of 0.5, as a result of which the carbon number of the whole molecule is decreased by unity.

The effective carbon number of an organic molecule thus determines the character and the degree of oxidation of the molecule and can serve as a criterion for the identification of either individual compounds or classes of substances.

Within one homologous series an increase in the number of carbon atoms is accompanied by an increase in the carbon number of the molecule and the molecular weight. A relatively little-varying parameter characterizing a substance of a given series is the ratio of the carbon number to the molecular weight. This ratio is characterized by the specific ionization efficiency in flame ionization detection. It is reasonable to use this quantity for the identification of classes of compounds.

One way to obtain the identification criterion is associated with the use of the preliminary weight separation of gases. As a separator, one can use a "gas balance" whose design is close to that of Nerheim's densimeter[14]. The gas leaving a chromatographic column and pure carrier gas are fed to the "gas balance" inlets. The "gas balance" outlet channels, as distinct from a densimeter, are not joined but connected to the inlets of two flame ionization detectors (Fig. 4)[15].

In the analysis of substances whose molecular weight differs from that of the carrier gas the flows are redistributed in the "gas balance" vertical chambers, which results in the lower outlet flow being enriched with the heavy component and the upper outlet flow with the lighter component. Two values of the peak height of the determined component can be obtained from the chromatograms of two flame ionization detectors:

$$h_1^x = A_x(Q_1 - k\Delta M_x C_x)C_x \tag{7}$$

$$h_2^x = A_x(Q_2 + k\Delta M_x C_x)C_x \tag{8}$$

where A_x is the sensitivity of the detectors to the determined components, Q_1 and Q_2 are the carrier gas flows in the half-channels of the "gas balance" working chamber, k is the "gas balance" constant and ΔM_x is the difference between the molecular weights of the substance and the carrier gas. In a similar way we can write the expression for the two peaks of a known substance (standard). From these equations is derived the expression for the identification criterion:

$$K = \frac{A_x}{\Delta M_x} \bigg/ \frac{A_{st}}{\Delta M_{st}} = \frac{(h_1^x + h_2^x)^2 (h_2^{st} - h_1^{st})}{(h_2^x - h_1^x)(h_1^{st} + h_2^{st})^2} \tag{9}$$

TABLE I

VALUES OF IDENTIFICATION CRITERIA AND EFFECTIVE CARBON NUMBERS OF HY-
DROCARBONS, ALCOHOLS AND ETHERS

Group	Substance	Identification criterion			Effective carbon number		
		He	H_2	Ref. 16	He	H_2	Ref. 16
Hydrocarbons	C_5H_{12}	1	1	—	5	5	—
	C_6H_{14}	1	1	1	6	6	6
	C_7H_{16}	1	1	1	7	7	7
	C_8H_{18}	1	1	—	8	8	—
Alcohols	CH_3OH	0.38	0.38	0.368	0.825	0.82	0.75
	C_2H_5OH	0.535	0.525	0.56	1.65	1.65	7.7
	C_3H_7OH	0.645	0.63	0.63	2.65	2.65	2.56
	C_4H_3OH	0.715	0.695	0.7	3.65	3.65	3.56
Ethers	$C_2H_5OC_2H_5$	0.645	0.64	0.59	2.85	2.85	3.0
	$C_4H_9OC_4H_9$	0.74	0.75	—	6.85	6.85	—

It is convenient to use light gases (hydrogen or helium) as the carrier gas and a hydrocarbon as the standard. In this instance $\Delta M \approx M$, and for most hydrocarbons the identification criterion is approximately unity. The presence of oxygen in the molecule of an unknown substance will reduce, in comparison with the corresponding hydrocarbon, the value of A_x and raise ΔM. This is why the identification criterion for oxygen-containing compounds should be noticeably lower than unity.

Table I shows the experimental values of the identification criterion and the effective carbon number for some hydrocarbons, alcohols and ethers, obtained when helium and hydrogen were used as the carrier gas, and also the values of these quantities calculated from the results of measuring the detection ionization efficiency, cited by Ettre[16]. Hexane was used as the standard in the experiments. When the effective carbon number of a compound, n_c^x, was calculated, it was taken into account that this value is proportional to the detector sensitivity to a given compound, i.e.

$$K = \frac{n_c^x}{\Delta M_x} \bigg/ \frac{n_c^{st}}{\Delta M_{st}} \tag{10}$$

The results of the measurements show that the identification criteria for oxygen-containing compounds differ markedly from unity. It is thus possible to distinguish these compounds reliably from hydrocarbons, i.e., to achieve the identification of groups. The individual identification criteria for alcohols differ from one another. It is therefore possible in principle to identify individual compounds. It is necessary to note that a high accuracy of measuring the identification criterion can be achieved if one takes into account the differences in the sensitivity of two flame ionization detectors and a possible dissymmetry of the "gas balance".

Another problem that can be solved with the use of flame ionization detection regularities is that of the identification of the individual hydrocarbons. The detection of each substance is characterized by the effective carbon number. For a number of

hydrocrbon classes this is approximately equal to the number of carbon atoms, N_c, in the molecule of a compound. The value of this quantity may be sufficient for the identification of a compound.

If the detection is performed simultaneously with a flame ionization detector and a densimeter, for each substance one can measure two peak heights from the two chromatograms:

$$h_{GDD} = K_{GDD} (M_x - M_0) C \tag{11}$$

$$h_{FID} = K_{FID} n_c C \approx K_{FID} N_c C \tag{12}$$

where K_{GDD} and K_{FID} are the detector constants and M_0 is the molecular weight of the carrier gas. Eqn. 11 applies to the densimeter and eqn. 12 to the flame ionization detector. From these equations it follows that

$$\frac{H_{GDD}}{h_{FID}} = \frac{K_{GDD}}{K_{FID}} \cdot \frac{M_x}{n_c} - \frac{K_{GDD}}{K_{FID}} \cdot \frac{M_0}{n_c} \approx \frac{K_{GDD}}{K_{FID}} \cdot \frac{M_x}{N_c} - \frac{K_{GDD}}{K_{FID}} \cdot \frac{M_0}{N_c} \tag{13}$$

As the molecular weight of a hydrocarbon, M_x, is approximately proportional to the number of carbon atoms in the molecule, N_c, $M_x/N_c \approx$ constant. From this follows a simple dependence relating the peak heights of the two detectors with the number of carbon atoms in hydrocarbon molecules:

$$\frac{h_{GDD}}{h_{FID}} \approx a - b \cdot \frac{1}{N_c}$$

Fig. 5 shows the experimental dependence of h_{GDD}/h_{FID} on $1/N_c$ for C_5–C_{11} n-alkanes. There is a good linear depenence, and one can achieve a satisfactory accuracy in determining the number of carbon atoms in the molecule of a compound, taking into account the possibility of rounding the experimentally found values to a whole number.
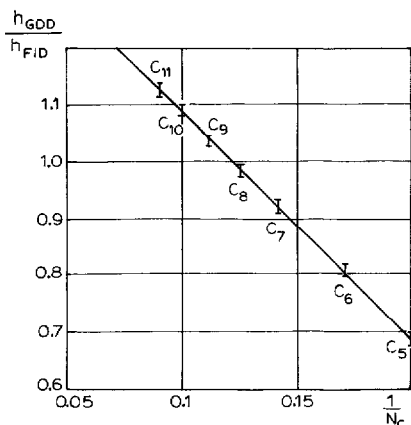

Fig. 5. Dependence of h_{GDD}/h_{FID} on $1/N_c$ for C_5–C_{11} n-alkanes.

It should be noted that in detecting aromatic compounds an anomalously high sensitivity is observed for the problems of substance identification.

CONCLUSIONS

In radioionization detection based on the Penning effect in neon, the phenomenon of anomalous weakening of the Penning effect by substances with high ionization potentials is observed if the carrier gas is contaminated with compounds that have low ionization potentials. This phenomenon is caused by significant participation of metastable (excimeric) neon molecules in the mechanism of the Penning effect. Anomalous phenomena of detection can be used to reproduce the actual detection conditions and the calibration graphs of detectors. They can also be used to identify individual substances.

The use of the combination of a flame ionization detector with a "gas balance" type of separator and a densimeter makes it possible to determine the specific ionization efficiency of flame ionization detection and the carbon numbers of organic compounds. It is possible to achieve the identification of classes of compounds and individual substances on this basis.

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