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NEW IONIZATION METHOD FOR THE DETECTION OF GASES AND VAPOURS

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SUMMARY

A new ionization method for the detection of gases and vapours is described. It is based on separation of the zone where the compound to be analyzed and the charge carriers interact from that where the useful signal is formed, so that optimum conditions are created in each of these zones. The construction of the detectors used is described and experimental data are presented. Some aspects of the sensitivity mechanism are considered. A physical model relying on a change in the mobility of the charge carriers after their penetration into the sensitive volume of the analyzed compound is proposed. Ion recombination is shown to contribute only slightly to the formation of the useful signal. Relationships between the magnitude of the space charge, recombination coefficient and charge carrier mobility and between the magnitude of the current in the signal formation zone, geometric dimensions of the ionization zone and gas supply mode are given. A formula for the reduced mobility of the charge carriers, taking into account the impurity concentration in the inert carrier gas, was derived. Finally, a relationship between the magnitude of the useful current signal, concentration of the analyzed compound and its electron affinity under the operating conditions selected and with the given detector design was obtained.

INTRODUCTION

Due to the fact that the solution of a variety of important practical problems could not be performed by means of an electron-capture detector, a new, recombination-free method has been developed¹. The method still possesses the known merits of the electron-capture technique but at the same time does not suffer from its intrinsic disadvantages such as the presence of the initial current caused by carrier-gas ionization and appearance of a signal due to ion recombination.

There is a contradiction between the electron density and the possibility of useful signal formation and registration. The reliability of this process depends on the electric field strength. With the electron-capture technique, even in the pulsed mode, this contradiction cannot be completely eliminated.

In the recombination-free method, which relies on the measurement of a change in the mobility of the charge after its penetration into the carrier gas containing the analyzed components, these disadvantages are no longer present, the

contribution of recombination to the process of signal generation being virtually zero.

EXPERIMENTAL

Fig. 1 shows the detector used with the recombination-free method². The lower part of the ionization chamber houses a connection (1) for the injection of the analyzed gas with a ^{63}Ni ionization source (2). This connection also serves as a potential electrode and is separated from the chamber by a ceramic sleeve. The upper part of the chamber accommodates an insulator-mounted measuring electrode (3) and a gas-outlet connection. The ionization zone (I) is defined by the potential electrode (1) and the ionization source (2), whereas the signal formation zone (II) is defined by these two electrodes. The detector was tested in a Gazokhrom 1106E chromatograph (U.S.S.R.). The glass column (1.5 m \times 3 mm I.D.) was filled with Chromaton N + 5% SE-30 stationary liquid phase. The detector parameters were determined by use of mixtures of γ -hexachlorocyclohexane (lindane) in hexane (10^{-6} mg/ml). The liquid samples were introduced with a Gazokhrom 101 microsyringe. Technical grade nitrogen was used as the carrier gas at a flow-rate of 80 ml/min. The temperatures of the column, evaporator and detector were 180, 200 and 230°C, respectively. The potential electrode supply voltage was 300 V.

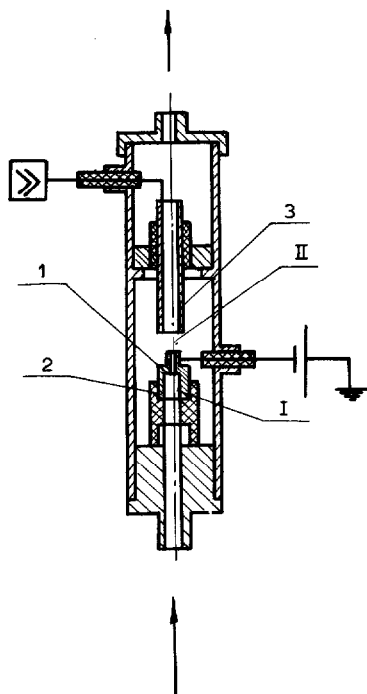


Fig. 1. Recombination-free two-electrode detector: I = ionization zone; II = signal formation zone; 1 = inlet connection for the analyzed gas (potential electrode); 2 = ionization source; 3 = measuring electrode.

The sensitivity threshold was calculated as

$$C_{\min} = 2(\Delta x)CVd/S \quad (1)$$

where Δx is the fluctuation noise level (mm); C is the concentration (mg/ml) of the analyzed compound; V is the volume (ml) of the compound injected; d is the chart feed rate (mm/s) and S is the peak area (mm²). The value of C_{\min} was found to be $5 \cdot 10^{-14}$ g/s.

The tests revealed that although the sensitivity threshold of the new detector is substantially lower than that of the electron-capture detector, its noise current is much larger than zero, which is attributed to the presence of undetectable impurities in the carrier gas, giving rise to negative ions, e.g., oxygen ones.

To decrease the initial current, a three-electrode detector was developed (Fig. 2)^{3,4}. Its construction is similar to that of the first one described except that the signal formation zone (II) has an additional self-powered annular electrode (4) generating a field in a plane transverse to the velocity vector of the ions ejected from the ionization zone (I) by the carrier-gas flow. Under the same conditions, the noise current was $2 \cdot 10^{-14}$ A and the sensitivity threshold for lindane was $1.5 \cdot 10^{-14}$ g/s.

RESULTS AND DISCUSSION

The new recombination-free analytical method can be described essentially as follows.

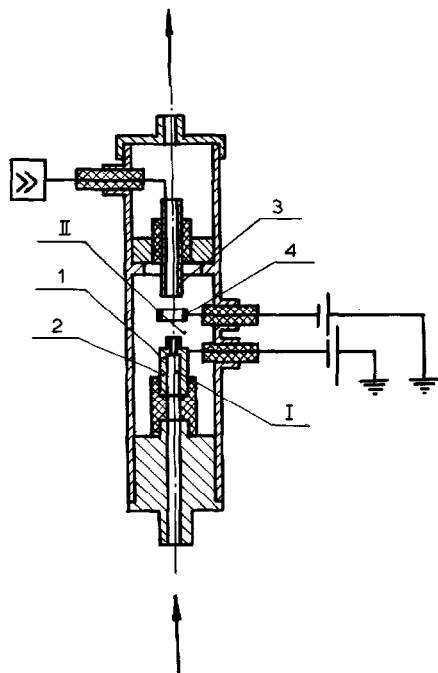


Fig. 2. Recombination-free three-electrode detector. Details as in Fig. 1, except 4 = additional annular electrode.

In the ionization zone (I, Fig. 1) the radioactive source (2) induces ionization of the inert carrier gas thereby creating a certain number of electrons and positive ions. The highly mobile electrons diffuse toward the surface of the earthed source and are neutralized there upon. The carrier gas flow-rate is selected such that the internal friction forces of the ionization zone (I) will not cause the ions to appear in the signal formation zone (II). Thus a positive space charge appears in the ionization zone (I), resulting in a very strong electric field.

The field strength can be calculated as

$$E = \frac{q}{2\pi r \epsilon_0 v_1 \tau} = \frac{ne}{2\pi r \epsilon_0 l} \quad (2)$$

where q is the magnitude (Coulomb) of the space charge generated in the ionization zone in unit time; n is the number of ions in the ionization zone; e is the charge (Coulomb) of an ion (electron), r is the radius (m) of the ionization zone, ϵ_0 is a constant equal to $8.85 \cdot 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$; v_1 is the gas flow-rate (m/s) in the ionization zone, τ is the constant measurement time (s) and l is the length (m) of the ionization zone. Since the number of electrons, n , and the number of charges formed in the ionization zone in unit time, N_0 , are related⁵

$$n = \sqrt{\frac{N_0}{\alpha}} \quad (3)$$

where α is the recombination coefficient (cm^3/s), and the ^{63}Ni β -radiation is nearly completely exhausted at a distance of 3 mm in nitrogen at atmospheric pressure, the space charge can be found from

$$q = e \sqrt{\frac{AwV_i}{I\alpha}} \quad (4)$$

where A is the activity (Bq) of the source, w is the mean energy (eV) of the β -particles, V_i is the volume (cm^3) of the ionization zone and I is the ionization potential (eV) of the carrier-gas atoms. From eqns. 2–4 we can write:

$$E = \frac{e \sqrt{\frac{AwV_i}{I\alpha}}}{2\pi r \epsilon_0 v_1 \tau} \quad (5)$$

Substituting into this equation the experimental values obtained ($A = 3.7 \cdot 10^8 \text{ Bq}$; $w = 2.2 \cdot 10^4 \text{ eV}$; $V_i = 0.216 \text{ cm}^3$; $I = 35.5 \text{ eV}$; $\alpha = 0.2 \cdot 10^{-6} \text{ cm}^3/\text{s}$; $v_1 = 0.076 \text{ cm/s}$; $\tau = 1 \text{ s}$), the field strength in the ionization zone I induced by the space charge is calculated to be $> 100 \text{ V/cm}$). This is sufficient for the collection of all the free electrons on the earthed ionization source (2).

Although the number of ions ejected into the signal formation zone (II) is also close to zero, the initial detector current differs from zero. It is generated by undetectable impurities in the carrier gas which give rise to negative ions. In practice, the

most representative impurity of this kind is oxygen. The analyzed compounds penetrating into the ionization zone (I) and having a positive electron affinity entrap the electrons to form negative ions of low mobilities. These partially recombine with the positive ions thereby significantly decreasing the magnitude of the space charge and, hence, the field strength in this zone. As a result, the remaining part of the negative ions of the ionized compound are ejected into the signal formation zone (II) by the internal friction forces. The number of ejected negative ions in this zone governs the magnitude of the useful current signal indicating the concentration of the analyzed compound.

By use of this physical model, one can obtain an equation for the decrease in the number of charges in the ionization zone (I) due to recombination, directed drift toward the walls of the connection (1) and diffusion⁶

$$\frac{dn}{dt} = N_0 - \alpha n_1 n_2 - \mu \cdot \frac{\Delta n}{\Delta x} \cdot E - D \cdot \frac{\Delta n}{\Delta x} \tag{6}$$

where n_1 is the instantaneous value of the negative ion concentration, n_2 is the instantaneous value of the positive ion concentration, μ is the ion mobility, $\Delta n/\Delta x$ is the gradient of ion concentration and D is the diffusion coefficient.

Since $\mu E \gg D$ and assuming that $n_1 = n_2 = n$, eqn. 6 can be rewritten as

$$\frac{dn}{dt} = N_0 - \alpha n^2 - \mu \frac{n}{r} \cdot \frac{ne}{2\pi lr \epsilon_0} \tag{7}$$

$$= N_0 - \alpha n^2 - \mu a n^2 \tag{8}$$

where:

$$a = e/2\pi lr^2 \epsilon_0 \tag{9}$$

By integration of eqn. 8, denoting the logarithmic constant as $\ln A$ and $\alpha + a\mu = \beta$ and then changing from logarithms to numbers, we obtain:

$$\frac{1 + \sqrt{\frac{\beta}{N_0}} \cdot n}{1 - \sqrt{\frac{\beta}{N_0}} \cdot n} = A e^{2t\sqrt{\beta N_0}} \tag{10}$$

$$1 - \sqrt{\frac{\beta}{N_0}} \cdot n$$

Hence, the relationship between the charge concentration and time is:

$$n(t) = \sqrt{\frac{N_0}{\beta}} \cdot \frac{A - e^{-2t\sqrt{\beta N_0}}}{A + e^{-2t\sqrt{\beta N_0}}} \tag{11}$$

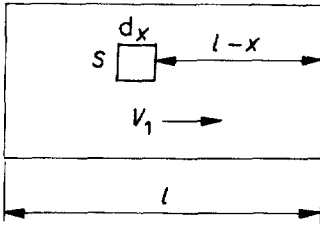
Denoting the initial number of ions per unit volume by n_0 and assuming (at $t = 0$) $n = n_0$, the constant A is defined as:

$$A = \frac{\sqrt{\frac{N_0}{\beta}} + n_0}{\sqrt{\frac{N_0}{\beta}} - n_0} \quad (12)$$

At $t \rightarrow \infty$, number of ions, n_∞ , is:

$$n_\infty = \sqrt{\frac{N_0}{\beta}} \quad (13)$$

Knowing the relationship $n(t)$, one can calculate the current magnitude in the signal formation zone (II), which is proportional to the magnitude of the charge ejected from the ionization zone (II) in unit time:



The carrier gas volume, Sdx , at time $t = 0$ is separated from the exit cross-section of the connection (1) by the distance $l-x$. This volume will reach the exit cross-section in a time $(l-x)/v_1$, the density (concentration) will change in this time and the area, S , of this cross-section will receive $Sn(t)dx$ charges, *i.e.*, $n [(l-x)/v_1]dx$ charges per unit area.

Upon integrating over the entire length of the ionization zone (I), one obtains the total charge which passes through the exit cross-section per unit area in time l/v_1 . Therefore the current, I_0 , passing through the cross-section can be expressed as:

$$I_0 = \frac{v_1}{l} \int_0^l n \left(\frac{l-x}{v_1} \right) dx = \frac{v_1}{l} \int_0^l \sqrt{\frac{N_0}{\beta}} \cdot \frac{A - e^{-2[(l-x)/v_1] \sqrt{\beta N_0}}}{A + e^{-2[(l-x)/v_1] \sqrt{\beta N_0}}} dx \quad (14)$$

As a result of integration we obtain:

$$I_0 = \frac{v_1^2}{2\beta l} \left[-2 \frac{\sqrt{\beta N_0}}{v_1} + 2 \ln \left(e^{\frac{2\sqrt{\beta N_0}}{v_1}} + 1 \right) - 2 \ln 2 \right] \quad (15)$$

This equation is not very convenient for estimation of the experimental data. Using

$$\frac{2k\sqrt{\beta N_0}}{v_1} \gg 1 \quad (16)$$

eqn. 15 can be transformed into:

$$I_0 = v_1 \sqrt{\frac{N_0}{\alpha + \frac{e\mu}{2\pi r^2 l e_0}}} \quad (17)$$

In eqn. 17 the current magnitude in the signal formation zone (II) is a function of the carrier gas velocity, the number of ion pairs appearing per unit time and the volume, recombination coefficient and mobility.

In practice, the recombination coefficient, $\alpha \ll e\mu/2\pi r^2 l e_0$ therefore the current in the signal formation zone (II) is completely governed by changes in the mobility of the negative charge carrier. Generally, the negative charge carriers can be represented as free electrons with mobility μ_1 and ions with mobility μ_2 , when $\mu_1 \gg \mu_2$. If in the gas the electron and ion concentrations are C_1 and C_2 , respectively, the reduced (effective) mobility of the negative charge carrier, μ , will be:

$$\mu = \frac{\mu_1 \mu_2}{C_1 \mu_1 + C_2 \mu_2} \quad (18)$$

At present there is no precise formula for calculating ion mobility in pure gases, still less for estimating the mobility of a gaseous mixture. It should be noted that the mobility of a mixture depends largely on the properties of the mixture itself rather than on those of the ions^{7,8}. A change in the relationship between the mixture components results in a change in the ion mean free path. Loeb⁹ proposed an equation which allows for this change

$$\mu_{ab} = \frac{\mu_a \mu_b}{f \mu_a + (1-f) \mu_b} \quad (19)$$

where μ_{ab} is the reduced mobility of the mixture, μ_a , μ_b are the mobilities of the components a and b, respectively, and f is the relative content of component a in the mixture. This equation gives a good fit to experimental results for some of binary gaseous mixtures such as hydrogen and carbon dioxide, air and carbon dioxide, argon and oxygen, ammonia and air.

Eqs. 18 and 19 are practically identical, except that the former deals with concentrations of charges, C_1 and C_2 , the latter with those of the gas.

If we assume that $C_1 + C_2 = 1$ and

$$C_2 = \gamma f \quad (20)$$

where γ is the electron-capture coefficient, and substitute these values into eqn. 18, we obtain:

$$\mu = \frac{\mu_1\mu_2}{\mu_1\gamma f + \mu_2(1 - \gamma f)} \quad (21)$$

Thus, as a result of some assumptions and transformations, eqn. 21 is obtained which relates the reduced mobility of the negative charge carrier to the impurity concentration and electron-capture coefficient, *i.e.*, a quantity proportional to the electron affinity.

Substituting eqn. 21 into eqn. 17 gives an equation for the current magnitude in the signal formation zone (II), dependent on the concentration of the impurity, f , and its electron affinity, γ :

$$I_0 = v_1 \sqrt{\frac{N_0}{\alpha + \frac{e\mu_1\mu_2}{2\pi r^2 l \epsilon_0 [\mu_1\gamma f + \mu_2(1 - \gamma f)]}}} \quad (22)$$

In the case of pure inert gases, *i.e.*, when $f = 0$, $\alpha \ll e\mu_1/2\pi r^2 l \epsilon_0$. Then

$$I_1 = v_1 r \sqrt{\frac{2\pi l \epsilon_0 N_0}{\mu}} \quad (23)$$

and the differential (useful) signal, ΔI , is:

$$\Delta I = v_1 K \left[\sqrt{\frac{\mu_1\gamma f + \mu_2(1 - \gamma f)}{2\pi r^2 \alpha l \epsilon_0 + e\mu_1\mu_2}} - \sqrt{\frac{1}{\mu_1}} \right] \quad (24)$$

where:

$$K = r \sqrt{2\pi l \epsilon_0 N_0} \quad (25)$$

Generally, eqn. 24 expresses the dependence of the useful signal on the concentration of the analyzed compound and its electron affinity at a given gas supply rate, v_1 , and constructional parameters (N_0 , r , l). This equation does not include a dependence on temperature whose change, however, substantially affects N_0 . Naturally, this equation does not permit calculations of the compound concentration from the current, but indicates only how they are related. Due to the fact that N_0 has differing values, the detector requires calibration. Nevertheless, the equation is of practical significance because it allows the designer to select the construction and geometrical dimensions, type of ionization chamber and activity of the source.

As is seen from eqn. 24, the useful current is linearly related to the concentration of the analyzed compound, which is a serious disadvantage of the recombination-free method. However, because of a lower initial current, compared with the

electron-capture detector, there will be a more favourable signal/noise ratio yielding a lower sensitivity threshold.

One remarkable feature of the recombination-free method is that its selectivity can be controlled both by selection of the carrier gas and conditions of the electric and gas supply.

When using air as carrier gas and in the presence of hydrocarbons, the method was able selectively to detect atrazine (at a level of $5 \cdot 10^{-13}$ g/s), whereas in the case of technical grade nitrogen the sensitivity threshold in respect of lindane was better than $2 \cdot 10^{-14}$ g/s.

The new method will find wide application where the sensitivity and selectivity of the electron-capture detector are insufficient for specific uses such as determination of the minimum acceptable concentrations of pesticides in the atmosphere.

CONCLUSIONS

(1) As a result of theoretical and experimental studies, a new, recombination-free, method for the analysis of gases and vapours is proposed. The sensitivity threshold of the method is lower than that of the electron-capture technique.

(2) The sensitivity mechanism is described and a relationship between the concentration of the analyzed compound, its electron affinity and the useful signal at the design parameters selected has been derived.

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