SOLUTION OF STEADY-STATE PROBLEM OF GAS CHROMATOGRAPHY

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A method of analyzing gas mixtures known under the name of gas chromatography has grown rapidly over the past 10-15 years (cf.[1]). In the method a fraction of the gas mixture which is to be analyzed is subjected to ionization and forced to pass across a potential difference in a neutral gas filler from a negative or grid electrode A to a collector B (Fig. 1). Since the mobility of different ions of a mixture may differ, the ions take different times to travel through the path L. As a result the mixture becomes separated in terms of ion type, and in a graph, for example, of the dependence of the current intensity through a device on transit time there will be characteristic peaks by means of which the presence of ions of a particular substance may be detected. The method is distinguished by a high level of sensitivity and, therefore, has found numerous applications, even in criminology.

The design of devices used in gas chromatography and the analysis of measurement results requires a numerical solution of the corresponding non-steady-state problem, which incorporates diffusion and other processes which occur in a mixture containing different types of ions and neutral conductors in an electric field. However, all the characteristic times for these processes are much less than the time it takes for the chromatographic peaks to become blurred. A solution of the non-steady-state problem can thus be constructed on the basis of the solutions of the steady-state problem [2].

Schematically, the statement of the steady-state problem we wish to solve is as follows [3]. A flow of thermally excited electrons is directed across a grid electrode A toward a collector B. The space between A and B is filled with an inert gas or nitrogen at atmospheric pressure p and contains a slight admixture of the substance which is under investigation, i.e., an electrophorus whose molecules are ionized through the adhesion of electrons to its surface. The device is usually constructed in such a way as to maintain a constant current J of the negative particles from the grid electrode to the collector. On the basis of some known concentration $N_e(0)$ of electrons on the grid electrode, it is necessary to find the distribution $N_e(x)$ in the interval $0 < x < L$, which, in turn, makes it easy to find the distribution of the ion concentration $N_i(x)$, the field $E(x)$, the potential drop $U = \int E ds$,

and so on. Proceeding in this way it is possible to compute, for example, the current-voltage characteristics of the device or, by solving an inverse problem, to determine from experiments values of the parameters which are required in order to interpret the chromatographic measurements.

The condition according to which the current must be constant may be written in the following form:

$$J = -D_e \frac{dN_e}{dx} - D_i \frac{dN_i}{dx} + v_e N_e + v_i N_i \qquad (1)$$

(N_e, v_e, D_e, and N_i, v_i, D_i are the concentration, diffusion rate, and diffusion coefficient of the electrons and ions, respectively).

Since the electric field E is extremely weak, whereas the device operates at atmospheric pressure, the ratio E/p is small and the following relations hold:

$$v_e = -\mu_e E, \; v_i = -\mu_i E \qquad (2)$$

(μ_e and μ_i are the mobility of the electrons and ions, respectively). Over a broad range of conditions, the quantities N_e and N_i are connected by the relation
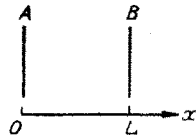
Fig. 1

$$N_i(x) = N_{i,0}[1 - \exp(-\alpha N_e(x))].$$ (3)

Here $N_{i,0}$ is the initial concentration of the electrophorus; $\alpha = 0.5k\tau$; k is the capture rate constant; and τ is the ion lifetime.

To this we must add Gauss' equation

$$\frac{dE}{dx} = -\frac{e}{\varepsilon_0}(N_e + N_i),$$ (4)

where e is electron charge and ε_0 is the permittivity of the gas filler.

This system of equations must be solved assuming the boundary condition

$$N_e(0) = N_{e,0}$$ (5)

($N_{e,0}$ is the known density of electrons on the grid electrode).

Let us present typical values of the parameters occurring in the system (1)-(4), taken from [3]: $N_{e,0} = 10^8$ cm^{-3}; $N_{i,0} = 10^8$ cm^{-3}; J in the range 10^{10}-10^{12} electrons/(cm^2·sec); $D_e = 10$ cm^2/sec; $D_i = 0.015$ cm^2/sec, $\mu_e = 13,500$ cm^2/sec; $\mu_i = 0.6$ cm^2/sec; $k = 2 \cdot 10^{-7}$ cm^3/sec; $\tau = 50$ msec; and L in the range 0.1-0.3 cm.

For the subsequent analysis it is important that the mobility and diffusion coefficient of the electrons be 10^3 greater than the corresponding ion quantities: $D_e \gg D_i$, $\mu_e \gg \mu_i$.

Since the system (1)-(4) reduces to a single second-order differential equation for $N_e(x)$, one more condition, which is not known precisely, is required. The following method was proposed in [3] to get around this difficulty.

If we start from the point x = 0, then, in order to solve the system we have to specify a value $N_e'(0)$. It turns out that if this value is not a happy choice, the solution $N_e(x)$ will either diverge or become negative with increasing x, whence the following prescription: Find an appropriate value $N_e'(0)$ by trial and error in order to succeed in "extending" the solution sufficiently far. This approach proves to be extremely time-consuming, as the authors of [3] themselves noted. Moreover, numerical instability imposes stringent constraints on the computational algorithm.

In the present article we propose a method of direct (i.e., without trial and error) solution of the problem we have stated.

Note that the approach of [3] is equivalent to specifying the missing second boundary condition in the form

$$N_e(x) \to 0 \text{ for } x \to \infty.$$ (5')

Therefore, in the asymptotic domain $x > x_0$ the condition $\alpha N_e \ll 1$ must hold. Because of this circumstance it is possible to simplify the system (1)-(4) to such an extent that it becomes possible to obtain analytically an approximate solution of the system. The exact system of equations is then integrated numerically, starting from a distant point x_0 in the direction of decreasing x. $N_e(x)$ meanwhile is increasing, since the solution must continue until the value $N_e(x) = N_{e,0}$ is reached. This point must also be taken as the coordinate of the grid electrode x = 0. If it turns out that the distance from the coordinate origin of the starting point $x_0 > L$, this will mean that the desired solution has been found, moreover, on the interval 0 < x < L. Otherwise, the approximate analytic solution must be used on the interval $x_0 < x < L$. Such is the outline of the approach we are proposing, which we also set forth in detail below.
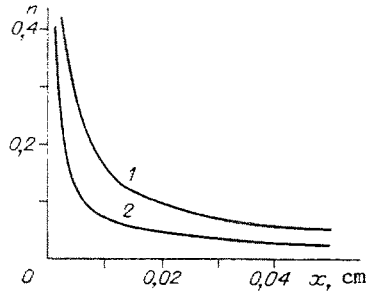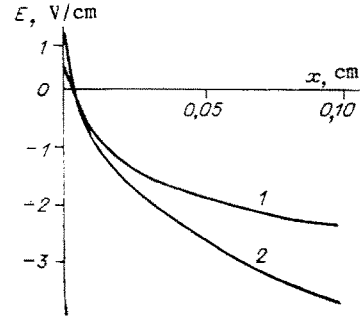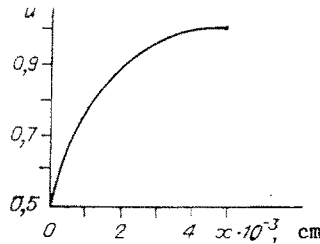
Fig. 2

Fig. 3

Fig. 4

Differentiating (1) with respect to x and eliminating the variables E, E', and N_i from the resulting equation by means of (1)-(4), we have for $N_e(x)$

$$N_e N_e'' = f(N_e, N_e').$$ (6)

The explicit form of the function f is not presented, since it is cumbersome and its derivation is transparent. Note that the factor of the leading derivative N" tends to zero with increasing x, whence the computational difficulties in the implementation of the approach of [3].

In the asymptotic domain $(x > x_0)$ we obtain using an approximation of (6) which is linear with respect to αN_e the following:

$$N_e N_e'' = (\alpha^2 D_i N_{i,0} N_e' + J N_e' + D N_e'^2 + a N_e^2)/D \equiv f_1(N_e, N_e').$$ (7)

Here

$$a = \frac{e}{\varepsilon_0} \mu (1 + \alpha N_{i,0}), \quad D = D_e + \alpha N_{i,0} D_i, \quad \mu = \mu_e + \alpha N_{i,0} \mu_i.$$ (8)

The first term in f_1, i.e., on the right-hand side of Eq. (7), may be omitted in view of condition (5') and the relation $D_e \gg D_i$.

In (7) let us pass to dimensionless variables, making the substitution of variables $\xi = x/\ell$, where the characteristic length $\ell = (a/D)^{1/2}$. Note that for the typical values of the parameters presented above, this length is on the order of 10^{-3} cm, whence $L \gg \ell$, which also suggests an "asymptotic" approach to the solution.

After the passage to dimensionless variables, we arrive at the following equation:

$$yy'' - y' - \beta y'^2 - y^3 = 0,$$ (9)

where $y(\xi) = N_e(x)$; $\beta = J\ell/D$.

Equation (9) may be integrated once, yielding

$$y' = -\beta \pm [2y^2(y + \beta(\xi - \xi_0))]^{1/2}$$ (10)

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(ξ_0 is the constant of integration, which has the sense of some conditional reference point occurring in the asymptotic solution of Eq. (7)). Let us set $z = \xi - \xi_0$. From (5') it follows that in (10) a positive value must be chosen for the root. Then, in a first approximation in negative powers of z, we find from (10) that

$$y(z) \approx y_1(z) = (\beta/2z)^{1/2}.$$

The second approximation $y_2(z)$ may be obtained if it is sought in the form $y_2 = y_1 + Az^{-b}$ (A and b are constants). This yields

$$y_2(z) = (\beta/2z)^{-1/2} - 0.5/z^2. \tag{11}$$

Hence follows a method of determining the initial values

$$N_e(x_0) = N_s, \quad N_e'(x_0) = N_s'$$

for the numerical solution of Eq. (7).

1. Let us specify N_S in such a way that the condition $\alpha N_S \ll 1$ is fulfilled. In the numerical experiments it turns out that it suffices to set $\alpha N_S = 0.1$. Let us now set $y_2 = N_S$ in (11).

2. Using the value of y_2 we find from (11) the auxiliary variable z. In order to obtain a good approximation of (11) the first term in (11) must be must greater than the second term, exceeding it by, for example, a factor of 10. If this is not the case, the value of N_S which has been specified must be reduced. Thus, the domain within which the approximate asymptotic solution of Eq. (7) is valid is found automatically.

3. The derivative N_S' may then be obtained either from (10) or by differentiation of (11) with respect to x.

Once the initial values of N_S and N_S' are known, we numerically integrate Eq. (6) in the direction of decreasing x until $N_e = N_{e,0}$. It must be kept in mind that near the grid electrode the density $N_e(x)$ varies extremely sharply. Therefore, in certain cases it is best to use an effective spline collocation technique with specially selected nodes in order to improve the accuracy of the numerical integration.

Of particular importance in the selection of the initial point x_0 (more precisely, in the selection of N_S) is the extent to which the asymptotic equation (7) is itself valid at that point, i.e., the extent to which the right-hand sides of Eqs. (6) and (7) coincide when N_S and N_S' are replaced. Numerical experiments and simple estimates show that the relative discrepancy

$$\delta = |f - f_1|/f$$

at the initial point may be significant in the case of high J, reaching several dozen percent, which, of course, will have a slight influence on the solution, inasmuch as in the asymptotic domain the right-hand sides of both equations are both small. But for the sake of achieving reliable results it is necessary to eliminate this shortcoming. For this purpose in (6) it is necessary to perform an expansion in powers of αN_S up through quadratic terms inclusively, thereby a refined analog of Eq. (7) or its dimensionless variant (9), and obtain an approximate solution y_{2a} which improves (11). After rather unwieldy computations, we obtain

$$y_{2a} = y_2(z) + \gamma/z, \quad \gamma = 0.25\alpha^2 N_{i,0}\beta/(1 + \alpha N_{i,0}). \tag{11a}$$

The use of (11a) yields a value $\delta < 0.005$ when $\alpha N_S = 0.1$ in the worst of the tested variants.

Naturally, questions arise as to how far should the initial point x_0 be and how reliable are the results obtained. At an initial level $\alpha N_S = 0.1$ in different trial computations, the point x_0 turns out to occur at a distance from 0.02 to 0.25 cm from the grid electrode, which is either less than the distance to the collector L or exceeds it by more than just a few centimeters. The accuracy of the solution was checked, first by varying the initial level N_S and the step of the numerical integration. Second, we may solve, not Eq. (6), in

which conservation of current J is explicitly stated, inasmuch as Eq. (1) is used to eliminate the field strength from the equations, but rather the system of equations (1) and (4) directly. It then becomes possible to control the conservation of current J when substituting into (1) the numerical solutions for $N_e(x)$ and $E(x)$ and the derivatives of these variables. Trial computations show that, given reasonable values of the computational parameters, the method yields an accuracy to four or five places.

Note that the parameters D and μ occurring in (8) depend very slightly on the characteristics of the ion component. Consequently, the solution $y(\xi)$ will depend very slightly on them far from the grid electrode and, since $L \gg \ell$, it might be expected that an admixture of ions would have to be detected mainly in terms of the variation in the characteristic length ℓ. Calculations that have been performed which involved varying the initial concentration of ions while keeping the other parameters invariant confirm the above scale invariance.

As an illustration, Figs. 2 and 3 present results obtained for a relative density of electrons $n = N_e(x)/N_{e,0}$ and of the field E in the case $J = 10^{11}$ electrons/(cm$^2 \cdot$sec) and $N_{e,0} = 10^8$ cm^{-3}. Curves 1 and 2 correspond to $N_{i,0} = 10^8$ and 10^9 cm^{-3}, respectively. The initial points for $\alpha N_s = 0.05$ are at distances of 0.41 and 0.31 cm, respectively. In both cases the standard Runge–Kutta method of numerical integration ensures conservation of current up to 0.02%. The characteristic lengths $\ell_1 = 1.65 \cdot 10^{-3}$ cm and $\ell_2 = 0.83 \cdot 10^{-3}$ cm.

Figure 4 illustrates the case of scale invariance, i.e., as $N_{i,0}$ is varied, the ratio

$$u = (n_1/n_2):(l_1/l_2)$$

differs significantly from 1 at x = 0, though with increasing x it rapidly approaches 1.

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