

SORPTION OF RADIOACTIVE SUBSTANCES IN CHROMATOGRAPHIC COLUMNS

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An analytical expression is derived for the steady-state concentration distribution of a radioactive substance in the gaseous phase along a column for a linear adsorption isotherm. Mass transport in the gas at the surface of the sorbent grains and diffusion inside the grains are taken into account. The temperature dependence is examined.

Dynamic adsorption of radioactive substances in sorption columns is accompanied by their simultaneous decay, which results in differences from the usual process. In this case a steady state is established in which the concentration of radioactive substance decreases along the column.

Some examples of dynamic sorption of radioactive substances have been considered in the literature. In [1] the concentration distribution of a radioactive gas over an adsorbent and at its surface was calculated in the steady state for an "everlasting gas adsorber". Also examined was the change of concentration of the radioactive substance in the gas phase and at the surface of the adsorbent during establishment of the steady state. Misin [2] derived an analytical expression for the steady concentration distribution of a radioactive substance in the gas along the length of an activated charcoal column. Diffusion of the substance in the gas phase at the surface of the adsorbent grains was allowed for, but the rate of diffusion inside the grain was assumed sufficiently great, and the diffusion effect in the material of the grain was not taken into account. However, in most cases of gas chromatography, the decisive process is diffusion in the sorbent grain. For small diffusion rates inside the grain Misin proposed an analogy with catalytic reactions [2].

In this paper a general expression is derived for dynamic adsorption of radioactive substances with a linear adsorption isotherm; then a study is made of the case when owing to the small diffusion rate, adsorption in the sorbent is comparatively slow. For many substances this occurs when the coefficient of internal diffusion is sufficiently small.

In deriving the equation it is assumed that the adsorption isotherm is linear and, consequently, that the adsorption coefficient does not depend on the concentration of radioactive substance in the gas. In addition, the heating effect due to radioactive decay is not considered. This effect was noted in [3, 4].

The initial equation, taking into account the change in the amount of substance per unit volume of column due to entrainment by the gas flow and radioactive decay, is written

$$\frac{\partial(Q + \kappa c)}{\partial t} = v \frac{\partial c}{\partial x} - \lambda(Q + \kappa c), \quad (1)$$

in the steady state

$$v \frac{dc}{dx} - \lambda(Q + \kappa c) = 0, \quad Q = n \int_V adV. \quad (2)$$

The equation for diffusion inside the grain, with account for radioactive decay, is

$$D \Delta a - \lambda a = \frac{\partial a}{\partial t}.$$

For steady-state conditions

$$D \Delta a - \lambda a = 0; \quad (3)$$

at the grain boundary

$$a(r_0) = c_1 \cdot \Gamma. \quad (4)$$

Solution of the system of equations (1)-(3) gives the concentration distribution of the substance in the gas along a charcoal column for steady-state conditions. We assume that the sorbent grains are small spheres of radius r_0 .

In spherical coordinates equation (3) becomes

$$D \left(\frac{d^2 a}{dr^2} + \frac{2}{r} \frac{da}{dr} \right) - \lambda a = 0, \quad (5)$$

and (2) will have the form

$$Q = n \int_0^{r_0} a(r) 4\pi r^2 dr. \quad (6)$$

Solving (5) with boundary condition (4), assuming that the solution is finite at all points of the volume, we obtain the function

$$a_{\text{sph}}(r) = \frac{r_0}{r} \frac{\text{sh}(r\sqrt{\lambda/D})}{\text{sh}(r_0\sqrt{\lambda/D})}. \quad (7)$$

The quantity $(D/\lambda)^{1/2}$ has the dimension of length and serves as a measure of the penetration of the radioactive substance into the sorbent grain. If $(D/\lambda)^{1/2} \gg r_0$, then $a(r) \cong a(r_0)$, i.e., the distribution in the grain is uniform. When $(D/\lambda)^{1/2} \ll r_0$ the substance is concentrated in the surface layer of the grain and does not reach the inner layer, since it manages to decay along the way.

We will find the relation between the concentration in the gas phase over the sorbent c and the concentration in the sorbent a . It is obtained from the equality of the mass flux densities on either side of the sorbent surface:

$$\beta(c - c_1) = D \left(\frac{da}{dr} \right)_{r=r_0}. \quad (8)$$

From conditions (4) and (8) we arrive at

$$a_g(r_0) = \beta c \left[\frac{\beta}{\Gamma} + \frac{\lambda}{3} r_0 E_g \left(r_0 \sqrt{\frac{\lambda}{D}} \right) \right]^{-1},$$

where

$$E_{\text{sph}}(r_0 \sqrt{\lambda/D}) = \frac{3}{r_0 \sqrt{\lambda/D}} \left[\text{cth } r_0 \sqrt{\lambda/D} - \frac{1}{r_0 \sqrt{\lambda/D}} \right]. \quad (9)$$

In accordance with (6) we obtain

$$Q_{\text{sph}} = c \frac{3\Gamma\beta E_{\text{sph}}(r_0 \sqrt{\lambda/D})}{3\beta + \lambda\Gamma r_0 E_{\text{sph}}(r_0 \sqrt{\lambda/D})} \frac{4}{3} \pi r_0^3 n.$$

The quantity $4/3 \pi r_0^3 n = 1 - \kappa$, by definition. Substituting Q_{sph} in (1) and solving, we find the concentration c as a function of x :

$$c_{\text{sph}}(x) = c_0 \exp \left\{ -\frac{\lambda}{v} \left[\frac{3\Gamma\beta E_{\text{sph}}(r_0 \sqrt{\lambda/D})}{3\beta + \lambda\Gamma r_0 E_{\text{sph}}(r_0 \sqrt{\lambda/D})} (1 - x) + x \right] x \right\}. \quad (10)$$

If it is assumed that the grains are cylinders of radius r_0 and length l , and diffusion through the ends of the cylinder can be ignored (sufficiently long cylinder), then the concentration distribution will have a somewhat different form. Thus, in cylindrical coordinates (3) is written as follows:

$$D \left(\frac{d^2 a}{dr^2} + \frac{1}{r} \frac{da}{dr} \right) - \lambda a = 0, \quad (11)$$

and (2) becomes

$$Q = nl \int_0^{r_0} a(r) 2\pi r dr. \quad (12)$$

The solution of (11), taking the account of the boundary condition and the finiteness condition, is the function

$$a_{\text{cyl}}(r) = \frac{a(r_0)}{I_0(r_0 \sqrt{\lambda/D})} I_0(r \sqrt{\lambda/D}). \quad (13)$$

Equation (13) has the same properties as (7).

From (4) and (8), we find $a_{\text{cyl}}(r_0)$:

$$a_{\text{cyl}}(r_0) = \beta c \left[\frac{\beta}{\Gamma} + \frac{\lambda}{2} r E_{\text{cyl}} \left(r_0 \sqrt{\frac{\lambda}{D}} \right) \right]^{-1},$$

where

$$E_{\text{cyl}}\left(r_0 \sqrt{\frac{\lambda}{D}}\right) = \frac{2}{r_0 \sqrt{\lambda/D}} \frac{I_1(r_0 \sqrt{\lambda/D})}{I_0(r_0 \sqrt{\lambda/D})}. \quad (14)$$

From (12) and (4) we obtain

$$Q_{\text{cyl}} = c \frac{2\Gamma\beta E_{\text{cyl}}(r_0 \sqrt{\lambda/D})}{2\beta + \lambda\Gamma r_0 E_{\text{cyl}}(r_0 \sqrt{\lambda/D})} \pi r_0^2 l n.$$

By definition $\pi r_0^2 l n = 1 - \kappa$. Finally, the concentration distribution along the column for cylindrical sorbent grains is:

$$c_{\text{cyl}}(x) = c_0 \exp\left\{-\frac{\lambda}{v} \left[\frac{2\Gamma\beta E_{\text{cyl}}(r_0 \sqrt{\lambda/D})}{2\beta + \lambda\Gamma r_0 E_{\text{cyl}}(r_0 \sqrt{\lambda/D})} (1-x) + \kappa \right] x\right\}. \quad (15)$$

It is obvious that for cylindrical grains the distribution will be intermediate between the case of spherical grains (equation (10)) and the case of equation (15).

The latter are not so very different from each other. Graphical forms of the functions $E_{\text{sph}}(r_0 \sqrt{\lambda/D})$ and $E_{\text{cyl}}(r_0 \sqrt{\lambda/D})$ are given in [5]. When $\sqrt{D/\lambda} \gg r_0$, the function $E \rightarrow 1$, which corresponds to a high rate of diffusion inside the grain and deep penetration of the radioactive substance. When $\sqrt{D/\lambda} \ll r_0$ the functions have the form

$$E_{\text{sph}}\left(r_0 \sqrt{\frac{\lambda}{D}}\right) \cong \frac{3}{r_0 \sqrt{\lambda/D}}; \quad E_{\text{cyl}}\left(r_0 \sqrt{\frac{\lambda}{D}}\right) \cong \frac{2}{r_0 \sqrt{\lambda/D}}.$$

In this case, as we have already pointed out, the radioactive substance lies near the surface of the grain in a thin layer. The depth of penetration is small.

If $\beta \gg \lambda\Gamma r_0 E(r_0 \sqrt{\lambda/D})$ and the second term in the square brackets κ can be neglected in comparison with the other terms, then the expression for the concentration distribution is simplified and becomes

$$c(x) = c_0 \exp\left\{-\frac{\lambda}{v} \Gamma E(r_0 \sqrt{\lambda/D}) (1-x)x\right\}. \quad (16)$$

This corresponds to the case when the decisive stage of the process of mass transfer into the grain is internal diffusion.

In (10) and (15) the concentration distribution of radioactive substance in the gas phase along the column is a function of temperature, since the adsorption coefficient Γ and the diffusion coefficient D are temperature-dependent. Knowing these dependences, it is possible to consider how the concentration distribution varies with temperature. We assume that the adsorption and diffusion coefficients depend on temperature as follows:

$$\Gamma(T) = A \exp(q/RT) T/T_0, \quad (17)$$

$$D(T) = B \exp(-\varepsilon/RT). \quad (18)$$

We will use (16) and consider first the case when $E(r_0 \sqrt{\lambda/D}) = 1$. Then

$$c = c_0 \exp\left\{-\frac{\lambda\Gamma}{v} (1-x)x\right\}.$$

Substituting for Γ from (17), we obtain

$$c = c_0 \exp\{-\alpha_0 T \exp[q/RT]\}, \quad (19)$$

i. e., the concentration distribution changes sharply with temperature. The lower the temperature, the steeper the drop in concentration along the column.

In the other extreme case, when $\sqrt{D/\lambda} \ll r_0$

$$c_{\text{sph}}(x) = c_0 \exp\left\{-\frac{3\Gamma \sqrt{\lambda D}}{v r_0} (1-x)x\right\}.$$

Substituting (17) and (18), we get

$$c_{\text{sph}} = c_0 \exp\left\{-\alpha_1 T \exp\left[\frac{1}{RT} \left(q - \frac{\varepsilon}{2}\right)\right]\right\}.$$

For shallow penetration of the radioactive substance into the sorbent the temperature dependence is less pronounced than that given by (19).

NOTATION

x - coordinate along column axis; $c(x)$, $c_1(x)$, and c_0 - concentration of radioactive substance in the gas, in a thin layer of gas surrounding the adsorbent grain, and in the gas at the column inlet; κ - fraction of gas phase in working volume of column; r - radial coordinate of sorbent grain; $a(r, x)$ - concentration of radioactive substance in sorbent grain; r_0 and l - dimensions of sorbent grain; n - number of grains per unit volume of column; $Q(x)$ - quantity of radioactive substance sorbed per unit volume of column; $\Gamma(T)$ - adsorption coefficient, i. e., ratio of concentration of sorbed substance in state of equilibrium in sorbent to its concentration in the gas phase over the sorbent at the same temperature as the sorbent; $D(T)$ - effective diffusion coefficient in sorbent grain; β - mass transfer coefficient; q - heat of adsorption; ε - activation energy; R - gas constant; T - absolute temperature ($T_0 = 273^\circ\text{K}$); v - effective gas flow rate in column (flow referred to unit cross section of column); λ - radioactive decay constant; I_0 and I_1 - zero and first-order Bessel functions with imaginary argument; A , B , α_0 , and α_1 - constants.

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