DETERMINATION OF THE INITIAL IMPURITY CONTENT FOR A GAS MOVING IN A POROUS SORBENT

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Inverse problems are considered for the motion of an impurity in a carrier gas passing through a porous sorbent; the response function may be determined from output data along the inlet concentration.

The direct problem for an impurity moving in a carrier gas is to determine the concentration at the exit from a porous medium in terms of the known parameters of the medium and the input concentration. There are many papers on such topics [1-5]. Inverse problems are equally important, and these include the following: 1) determination of the input concentration from the known response of the medium and the measured output concentration; 2) determination of the response from the known concentrations at input and output; and 3) determination of the parameters of the porous medium. These aspects are considered here.

The linear approximation is used with constant diffusion coefficients and a constant kinetic sorption coefficient in discussing the physical processes for a gas moving in a porous column [6]; let $\varphi(\tau)$ be the concentration of the gas supplied to the column and $G(l, t)$ be the response; then the concentration at the output $u(l, t)$ is given by

$$u(l, t) = \int_0^t G(l, t-\tau)\varphi(\tau)\,d\tau. \tag{1}$$

Equation (1) is a Fredholm integral equation of the first kind of convolution type; the derivation of $\varphi(\tau)$ (or of $G(l, t)$) from (1) is therefore a problem of inverse type and requires the use of special methods.

Tikhonov [7, 8] laid the basis of the fundamental regularization method, which involves constructing an approximate solution to (1) (or to more general equations) by means of regularizing operators [9]. There are deterministic and nondeterministic (statistical) methods of constructing such operators. The statistical methods are convenient if the right side in (1) is a random function, as is the solution, and perhaps also the kernel. Examples are functions obtained by measurement. In some cases, statistical methods can provide an optimal solution to (1), including considerable improvement over the solutions obtained by deterministic methods [10]. Here we solve (1) by the method of [11], which provides a suboptimal solution that is acceptable in the presence of errors on the right and in the kernel of (1).

To determine $\Phi(\tau)$ from the known $u(l, t)$ by means of (1) we need to know $G(l, t)$; diffusion causes broadening, and the process is of nonequilibrium type, so we assume that a Henry sorption isotherm applies, and then the following analytic expression is obtained [6]:

$$\begin{gathered}
G(l, t) = G_1(l, t) + G_2(l, t),\\
G_1(l, t) = u_0(4\pi D t^3)^{-1/2}\exp\left\{-t(\lambda+\beta) - \frac{(l-\nu t)^2}{4Dt}\right\},\\
G_2(l, t) = u_0\beta l\gamma^{1/2}(\pi D)^{-1/2}\exp\{-t(\lambda+\beta\gamma)\}\times\\
\times\int_0^t \tau^{-1}(t-\tau)^{-1/2} I_1\left(2\beta\nu^{-1}\sqrt{\gamma\tau(t-\tau)}\right)\exp\left\{-\beta\tau(1-\gamma) - \frac{(l-\nu\tau)^2}{4D\tau}\right\}d\tau.
\end{gathered} \tag{2}$$

Here γ is the reciprocal of the Henry coefficient and u_0 is a constant.

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Expression (2) contains the parameters of the medium and impurity such as the diffusion coefficient D and the kinetic sorption coefficient β, on which no data are usually available, while no good methods of measurement exist either. It is therefore of considerable interest to be able to determine the response parameters by experiment. Here we show that the response function can sometimes be measured directly.

We first consider methods of determining the response and the conditions under which direct measurement is possible; let T_{in} be the length of the concentration pulse $\varphi(\tau)$ at the input, which is to be determined from (1). The response is essentially a Green's function for the corresponding Cauchy problem [6], so one expects that $G(l, t)$ can be measured directly if a δ pulse is applied to the input of length $t_{in} \ll T_{in}$, while t_{out} is the length of the pulse at the output (the length of the measured response). Numerical implementation is the most complicated when T^*_{in} is comparable with the duration of the response or $T^*_{in} \sim t_{out}$, and the condition $t_{in} \ll T^*_{in}$ may be put as

$$t_{in} \ll t_{out}. \tag{3}$$

Clearly, the measured response can be used to determine $\varphi(\tau)$ for any relation $T_{in} > T^*_{in}$ if this condition is met.

However, obedience to (3) alone is insufficient for direct measurement of $G(l, t)$ since (1) describes the transport by the gas on the assumption that a Henry isotherm applies; therefore, $G(l, t)$ should not be measured with an excessive input (large amount of impurity). If t_{in} is fixed, the second condition can be considered as a condition on the impurity concentration.

The acceptable limits to t_{in}/t_{out} and the upper bound to the input concentration have been derived from experiment; a given column length and given impurity level gave results for $G(l, t)$ that agreed to within 4% for t_{in}/t_{out} of 1/120, 1/60, 1/30; measurements were not made with higher values of the ratio, while lower values were difficult to realize. It was also found that the concentration of the added gas (xenon) could be as high as 6% for the 1/30 ratio.

The response function can also be determined in another way. The replacement $\varepsilon = t - \tau$ in (1) results again in a convolution:

$$u(l, t) = \int_0^t G(l, \xi)\,\varphi(t-\xi)\,d\xi, \tag{4}$$

but now for $G(l, \xi)$ with known $u(l, t)$ and $\varphi(\tau)$; one can measure the concentration at input and output to determine $G(l, \xi)$ by solving this equation. Numerical determination of the pulse response (response function) can be performed by regularization with fast Fourier transformation [12] from recordings of the input and output signals employed, although the method described in that paper was fairly complicated.

The parameters of the medium may be determined and the model may be compared with the actual processes governing the gas motion by fitting an analytical expression to (2); the integrand in (2) can be written as the product of two functions, each of which may have a distinct sharp peak as a function of the relevant parameters. If the diffusion coefficient D is small, i.e.,

$$D \ll lv, \tag{5}$$

the maximum in the integrand may be found by means of

$$\exp\left\{-\frac{(l-v\tau)^2}{4D\tau}\right\}.$$

In practice, (5) is usually met. The saddle-point method gives us from (2) that

$$G_2(l, t) = \frac{2\beta\sqrt{l\gamma}}{\sqrt{t-lv}}\, I_1\left(2\beta v^{-1}\sqrt{\gamma l(vt-l)}\right)\exp\{-\beta\gamma t v^{-1} - \beta v^{-1}(1-\gamma)t\}. \tag{6}$$

Also, (6) can be put in the following form via the asymptotic representation for a Bessel function of imaginary argument:

$$G_2(l, t) = A(l, t)\exp\{-(t-t_m)^2/(2\sigma_\beta^2)\}, \tag{7}$$

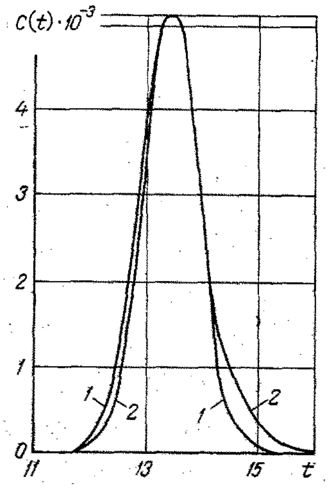

Fig. 1

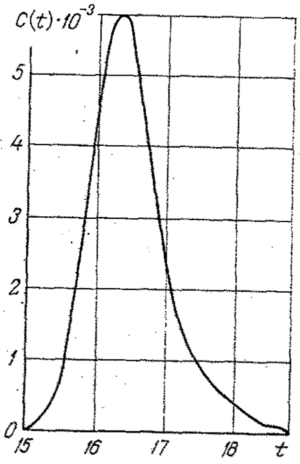

Fig. 2

Fig. 1. Comparison of 1) calculated response; 2) measured response; t in min.

Fig. 2. Response function measured in simulation.

where

$$A(l,\ t) = (\beta\nu\pi^{-1})^{1/2}(\gamma l)^{1/4}(\nu t - l)^{-3/4};\quad t_m = \frac{l(1+\gamma)}{\nu\gamma};$$

$$\sigma_\beta = (2\beta\gamma^2\nu)^{-1/2}\left(\sqrt{\gamma(\nu t - l)} + \sqrt{l}\right). \tag{8}$$

The other maximum in the integrand is determined by the second function $I_1(2\beta\nu^{-1}\sqrt{\gamma\tau(t-\tau)})\exp\{-\beta\tau(1+\gamma)\}$; the contribution to the integral of (2) from this maximum can be derived for $\beta t \gg (1+\gamma)^2[\gamma(\gamma-1)]$ by analogy with (7) with the value for t_m as in (8) but with the half-width

$$\sigma_D = \nu^{-1}\gamma^{-1/2}[2D(1+\gamma)t]^{1/2}. \tag{9}$$

For values $\beta t \gg 1$ the response $G(l,\ t)$ is determined by the $G_2(l,\ t)$ term, while the half-width is governed by the diffusion and the adsorption. The overall half-width of $G(l,\ t)$ is thus composed of the values from (8) and (9)

$$\sigma \simeq \sigma_\beta + \sigma_D. \tag{10}$$

If all the parameters of the medium and the impurity are known apart from the kinetic sorption coefficient β and the diffusion coefficient D, it is possible to determine β and D unambiguously from (10) because the half-width of the response increases with D and as β decreases, while any fall in β displaces the peak in the function.

For example, measurements were made with the parameters $\nu = 2.514$ cm/min, $l = 300$ cm, $\gamma = 0.60466$ and the response had $\sigma = 0.524$ min, whereupon (10) becomes

$$\sigma = 0.425 = 0.0334\sqrt{D} + 23.56/\sqrt{\beta}.$$

Fitting to the measured response gave $D = 77.1$ cm^2/min, $\beta = 6.4 \cdot 10^4$ min^{-1}.

Figure 1 shows examples of the measured and calculated response functions that indicate the fit of the model to the processes.

Although the response can be measured directly, analytical representation is of considerable importance, since it is possible to measure $G(l,\ t)$ for a column of length l_1 and then to derive the response for a column of length l_2, or alternatively to predict the features of a column for other values of the gas and filling parameters, especially in the design of columns with preset parameters.

We assume that $G(l,\ t)$ has been determined in order to discuss briefly the technique for solving (1) by the method of [11]. An approximate solution $\varphi(\tau)$ is sought in the form

$$\varphi(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{K(-\omega)U(\omega)}{K(\omega)K(-\omega) + R^2(\omega)} \exp(-i\omega t)\, d\omega, \tag{11}$$

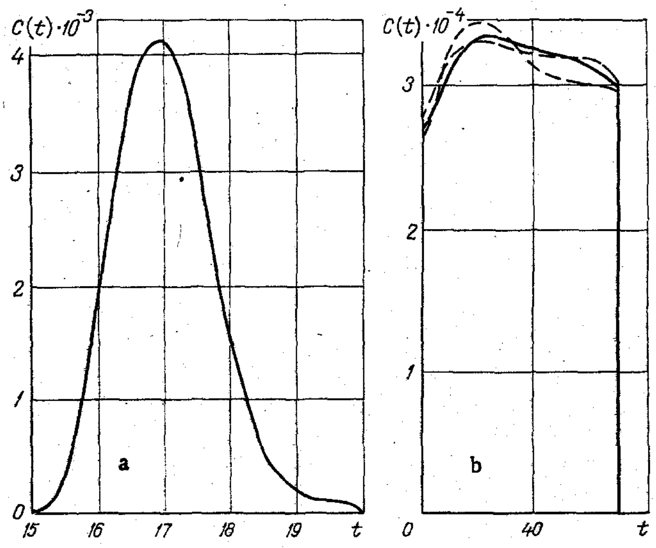

Fig. 3. Xenon concentrations: a) measured at outlet of porous column in model experiments; b) recovered for input of porous column from measured data.

where $K(\omega)$ and $U(\omega)$ are the Fourier transforms of $G(l, t)$ and $u(l, t)$ (parameter l has been omitted in the Fourier transforms), while the function $R^2(\omega) > 0$ is chosen to be such as to give a suboptimal solution stable in the presence of small perturbations in $u(l, t)$ and $G(l, \tau)$. The integral in (11) is replaced by an integral sum, and the variances of $K(\omega_i)$ and $U(\omega_i)$ are calculated at each step in the integration with respect to ω on the basis of the quadrature formula used for $U(\omega)$ and $K(\omega)$, where the number $R^2(\omega_i)$ is constructed in accordance with the following rule:

$$R^2(\omega_i) = \begin{cases} 3.5\,\sigma_i^2 + 2\delta_i^2\rho_i^{-2}, & \text{if } \eta_i \geqslant \alpha\delta_i \text{and} \, r_i \geqslant \alpha\sigma_i, \\ \infty, & \text{if } \eta_i < \alpha\delta_i \text{ or } r_i < \alpha\sigma_i, \end{cases} \qquad (12)$$

where

$$\delta_i^2 = \max\{D[\operatorname{Re} U(\omega_i)],\ D[\operatorname{Im} U(\omega_i)]\};$$

$$\sigma_i^2 = \max\{D[\operatorname{Re} K(\omega_i)],\ D[\operatorname{Im} K(\omega_i)]\};$$

in which D is the dispersion operator and $r_i = |K(\omega_i)|$, $\eta_i = |U(\omega_i)|$; $\rho_i = \eta_i/r_i$; the parameter $\alpha > 0$ is the cutoff parameter, which specifies the signal-to-noise ratio below which the contribution to the integral sum for (11) is discarded. Estimates [11] and practical calculations show that α lies in the range 2.0-4.5, and the error levels of $u(l, t)$ and $G(l, t)$ are known only approximately, so we can assume that $\alpha = 3$. More exact determination of the solution is possible if a priori information is available on the solution or on the modulus of the Fourier transform. For example, the desired solution may be continuous, in which case $\rho(\omega) = O(\omega^{-2})$, and therefore the weak-signal contribution can be incorporated by taking $R^2(\omega_i) = \alpha_i\omega_i^2$, where parameter α is derived from the condition for continuity of $\rho(\omega_i)$ vector.

Methods developed for defining $\varphi(\tau)$ have been applied to advantage in practical problems; an example is the processing of data from a simulation experiment in which a gas impurity was supplied to a column in accordance with a known relationship. The input concentration was

$$\varphi(\tau) = \begin{cases} \varphi_0 & 0 \leqslant t \leqslant T, \\ 0 & t > T. \end{cases}$$

The response function was measured as described above; the t_{in}/t_{out} ratio was 1/60. Figure 2 and Fig. 3a show the measured $G(l, t)$ and $u(l, t)$; no a priori information was used in solving (1).

A Tsvet-104 gas chromatograph was used to record the initial chromatograms; the measurements were made with a thermal-conductivity detector. Each column was of length 3 m and filled with synthetic NaX xeolite. The grain-size fraction 0.15-0.25 mm was used. The column was prepared by flushing with carrier gas for over 24 h (high-purity helium at 360°C), which eliminated adsorbed water and carbon dioxide. The measurements were made under isothermal conditions with the column at 50°C. The amounts used (0.25cm, 0.5, 5.0, and 33 cm^3) were dispensed with an error of 1%. The impurity was xenon diluted with helium, and the possible distortion in the emergent peak arising from overload was examined by using mixtures with xenon contents of 0.01, 0.1, and 1% by volume. A correction was also applied for the distortion of the peak on account of the finite detector volume. The characteristic and transit times for the sensitive volume of the catharometer were not more than 0.3 sec, and it was found that these sources of distortion could be neglected.

A characteristic feature of a Fourier transformation is that it cannot provide a close fit to a steep edge or (especially) a discontinuity in the function resulting from numerical inversion, and therefore to the solution of (1). Instead, one obtains rounded steps, and therefore the half-width of the solution increases, as does the length of the nonzero range. However, one can readily identify the region in which the solution actually is different from zero. If $u(l, t)$ differs from zero over the range $t \in [a, b]$, $G(l, t)$ does the same over $[c, d]$, and the solution is nonzero in the range $[a-c, b-d]$. The solid line in Fig. 3b shows the solution obtained with this method of identifying the nonzero region.

The error level in this solution arising from errors in $u(l, t)$ and $G(l, t)$ was estimated as follows: the measured functions $u(l, t)$ and $G(l, t)$ were corrupted with noise whose level was equal to the error level in the measurements (2%) by means of various sequences of random numbers, and $\varphi(\tau)$ was recovered for each of these. The broken lines in Fig. 3b show the recovery results, which indicate the error band. Only a priori information on the solution can give better results for the given error level.

NOTATION

$\varphi(\tau)$, input gas concentration; $u(l, t)$, output gas concentration; $G(l, t)$, response function; u_0, constant; D, diffusion coefficient; β, kinematic sorption coefficient; γ, reciprocal of the Henry coefficient; λ, radioactive-decay constant; l, column length; τ, integration parameter; T_{in}, length of $\varphi(\tau)$ pulse at the inlet; ν, gas flow velocity; $K(\omega)$ and $U(\omega)$, Fourier transforms of $G(l, t)$ and $u(l, t)$.

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