PHYSICAL CHEMISTRY

A. A. ZHUKHOVITSKII, L. M. LAPKIN, A. A. DATSEVICH

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. A. ZHUKHOVITSKII, L. M. LAPKIN, A. A. DATSEVICH

THE ZERO LINE IN VACANCY CHROMATOGRAPHY AS THE BASIS OF CONTINUOUS ANALYSIS WITHOUT DOSING

(Presented by Academician P. A. Rebinder, 30 XI 1964)

All known variants of chromatography are discontinuous, since they require either periodic dosing of the mixture being analyzed (or of the carrier gas), or cyclic delivery of the mixture (the thermodynamic method). It seems important to determine the possibility of continuous analysis without dosing. Such analysis is impossible within the framework of ordinary chromatography and, in principle, can be carried out on the basis of vacancy chromatography (1-4). However, in the published theory of vacancy chromatography (4), the question of the regularities that determine the drift of the zero line on the recorder when the composition of the mixture changes with time was not considered.

The purpose of the present work is to investigate these regularities and to analyze the possibility of continuous analysis without dosing on the basis of these regularities.

Let us first consider the case of a carrier-gas mixture—one component. If a mixture of carrier gas with one component is passed continuously in succession through the reference chamber of the detector, the column, and the measuring chamber of the detector, then, at constant composition of the mixture, a zero line is recorded on the recorder. With continuous change in concentration, the zero line will deviate, and the magnitude of this deviation—the distance between the points on the zero lines at constant and variable concentrations at a given moment of time (H)—is determined by the difference of the concentrations in the detector chambers.

The gas concentration in the reference chamber is equal to that entering at the given moment, while the gas concentration in the measuring chamber is equal to the concentration that entered the reference chamber earlier by a time equal to the retention time (t^y).

Thus,

$$H = h_t - h_{t-t^y}, \tag{1}$$

where h_t is the detector signal corresponding to the instantaneous concentration of the component.

If it is assumed that over the time t^y the rate of change of concentration is constant, then

$$H = \frac{dh}{dt}\,t^y. \tag{2}$$

If a mixture of carrier gas not with one, but with n components passes through the system, then the magnitude H is determined by the following expression:

$$H = \sum_{i=1}^{i=n} \frac{dh_i}{dt}\,t_i^y. \tag{3}$$

By integration, equation (3) can be brought to the form:

$$\int H\,dt = \sum_{i=1}^{i=n} h_i t_i^y + \sum_{i=1}^{i=n} h_{i0} t_i^y, \tag{4}$$

h_{i0} is the detector signal corresponding to the concentration at the time chosen as the zero point. $\int H dt = S$ is determined graphically by the area bounded by the zero lines at constant and variable concentrations.

Since equation (4) contains n unknown quantities h_i, in order to determine from the quantity S the concentrations of all components it is necessary to have n equations (4), i.e., it is necessary to use n columns with different packings.

In deriving equations (3) and (4) it was assumed that the time derivative of the concentrations of the components may be regarded as constant over the retention time of this component. Thus, the approximation under discussion may be regarded as the next approximation in comparison with ordinary chromatography, where in the zeroth approximation it is assumed that the concentration remains constant over the retention time. The requirement of constancy of the rate of change of concentration is probably satisfied for most practical problems.

The possibility of measuring the rate of change of concentration, which, as was shown above, is realized in vacantochromatography, makes it possible almost completely to eliminate the inertia of measurements and to proceed to continuous analysis.

We carried out experiments in order to check the applicability of equations (3) and (4) and to ascertain the possibility of using them for continuous non-dosing analysis. The equations (3) and (4) were checked using as an example a mixture of isobutane and n-butane in air.

For continuous variation of the concentration, a 1-liter buffer vessel was used, into which regulated amounts of carrier gas and of the gas under investigation were introduced. The total concentration of the mixture under investigation in the carrier gas—air—varied from 0 to 12%.

From the buffer vessel the mixture was directed into the comparison chamber of the detector, whence it entered the column and the measuring chamber of the detector. For detection a G-10 katharometer was used; the recording was made on an EPP-09 potentiometer.

The column, of length $L = 2$ m and internal diameter 4 mm, was packed with diatomaceous earth brick impregnated with 15% ether of oleic acid and triethylene glycol. The mixture was passed at a rate of 16 ml/min. The experiments were carried out at 20° C.

Since the zero line also has a considerable drift at constant concentration, during the experiments the zero line at constant concentration was checked every hour. For this purpose the flow was switched in such a way that the gas, bypassing the column, passed from the comparison chamber of the detector to the throttle, and then to the measuring chamber of the detector. Since the volume between the chambers is negligibly small, practically identical concentrations passed through both chambers.

To determine the concentrations at different instants, 1 ml of carrier gas was periodically dosed into the inlet of the column with a D-27 valve, as a result of which vacancy peaks of the components were recorded.

Our aim was to check equation (4), which includes the values of the signals h_i corresponding to instantaneous concentrations. The height of the vacancy maximum (h_{Bi}) depends not only on the concentrations at the instant of dosing the carrier gas, but also on the retention times and on the plate height:

$$h_{Bi} \sim \frac{h_i}{t_i^y \sqrt{H_i}}.$$

Since the plate heights of butane and isobutane are close, it may be assumed that

$$h_i \sim h_{Bi} t_i^y.$$

Thus, instead of equation (4) we obtain:

$$S \sim \sum_{i=1}^{i=h} h_{B_i} (t_i^y)^2, \quad \text{if } h_{i0} = 0.$$

Figure 1 shows the relationship between the quantities $[h_{B_1}(t_1^y)^2 + h_{B_2}(t_2^y)^2]$ and S. As is seen from the figure, there is a rectilinear dependence between these quantities, and the ascending branch (points denoted a) coincides with the descending branch (b), i.e., the data of Fig. 1 satisfy equation (4).

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 1

Fig. 2

The dependence between the quantities

$$\frac{\Delta\left[h_{B_1}(t_1^y)^2 + h_{B_2}(t_2^y)^2\right]}{t}$$

and H, shown in Fig. 2, also confirms equation (3). The quantities h_i, t_i^y, H, S, and t were taken from experimental data. Similar data were also obtained on a 2 m column packed with Inza brick impregnated with 20% dibutyl phthalate.

As a result of the work carried out, the physical meaning of the zero line in vacancy chromatography has been investigated. It has been shown that the distance between points on the zero lines at constant and variable concentrations, corresponding to a definite moment of time, is linearly related to the rate of change of the concentrations of the components, while the area bounded by the zero lines at constant and variable concentrations is equal to the sum of the products of the retention times and the detector readings corresponding to the instantaneous value of the concentrations. The experimental data agree with these equations.

In contrast to ordinary elution chromatography, vacancy chromatography makes it possible to determine not only concentrations but also the rates of their change, which provides a basis for carrying out a continuous, non-dosing method of analysis.

Moscow Institute
of Steel and Alloys

Received
28 XI 1964

REFERENCES

1. A. A. Zhukhovitskii, N. M. Turkel’ taub, DAN, **143**, No. 3, 646 (1962).
2. A. A. Zhukhovitskii, N. M. Turkel’ taub, *Neftekhimiya*, **2**, No. 6, 818 (1962).

3. Ch. N. Reilley, G. P. Hildebrand, J. W. Ashley, *Anal. Chem.*, **34**, No. 10, 1198 (1962).

4. A. A. Zhukhovitskii, N. M. Turkel' taub et al., *Zav. lab.*, No. 1, 8 (1963).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.