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Abstract

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VACANTOCHROMATOGRAPHY*

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At present chromatography is the principal method for the analysis of mixtures in the control of chemical production and in scientific research.

Fundamentally new possibilities arise when the motion of sorbed bands is replaced by the motion, in the sorbed layer, of a vacancy filled only with carrier gas.

Let a stream of carrier gas containing one component of a substance sorbed in a linear region move continuously through a sorbent. Let us introduce instantaneously into the stream a portion of carrier gas. Then a region free of sorbed substance will begin to move through the layer.

If the equations of dynamics (1) are written taking into account external diffusion and the finiteness of the sorption rate, and if the difference between the continuously supplied and the instantaneous concentration is introduced as a new variable, then all the equations and the initial and boundary conditions for the motion of the vacancy and of the band coincide completely. This means that the velocity of motion of the vacancy and the laws describing its spreading are identical with the laws for the motion of a band.

Let the analyzed mixture be passed continuously through the layer. After sorption equilibrium has been established on the adsorbent, let us introduce into the stream of this mixture a portion of carrier gas. If all the components are sorbed in the linear region, the advance of the vacancies in each of them proceeds independently of the others. Consequently, the detector will record as many vacancies as there are components in the analyzed mixture. The peak corresponding to each vacancy will contain all the components except one, recorded by the detector. If a compensation method of detection is used, i.e., if the analyzed mixture is passed through the comparison chambers, then each peak directly records the concentration of the individual components. Thus, although in vacantochromatography, unlike ordinary elution chromatography, no separation of the mixture into individual components takes place, the analysis, calibration, etc., are identical. It is assumed here that the registration of components by the detector is additive.

As an illustration, Fig. 1a presents a vacantochromatogram of a mixture containing isobutane and butane (carrier gas nitrogen), on a tube ($L = 1.7$ m, $a =$

566 cm/min, $d = 2$ mm), filled with Inza diatomaceous brick impregnated with dinonyl phthalate (25%). A G-14 katharometer was used as the detector. The vacantochromatogram was obtained as a result of continuously passing the analyzed mixture through the layer and a single introduction of a portion of nitrogen.

Figure 1b shows an ordinary chromatogram for the same system, practically coinciding with the vacantochromatogram. In both cases the peak width should depend neither on the concentration of the component in the mixture nor on the amount of mixture or solvent introduced, provided this amount is not too large. The height of the maximum in both cases depends in the same way on the size of the sample of the mixture or carrier gas.

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* M. Gayer and M. N. Lagashkina took part in the experimental work.

Vacancy chromatography in the form described has one fundamental practical advantage over gas chromatography. Since the mixture being analyzed is passed directly through the sorbent layer, and dosing is carried out by the volume of the carrier gas, the dosing operation is sharply simplified. The need to use special materials, the possibility of overheating of the dosing device, etc., disappear.

However, the advantages of vacancy chromatography are not exhausted by this. It is known that a substantial limitation on the use of gas-adsorption chromatography is the spreading caused by the curvature of the isotherm. We shall show that in the new method this spreading is sharply reduced. It is known that the rate of movement of a given concentration is determined by the value $\partial a/\partial c$ (^{2}), where a is the amount of sorbed substance and c is the concentration. For definiteness, let us consider the case of the Langmuir isotherm:

$$a_i = \frac{\Gamma_i c_i}{1 + \Gamma_i c_i + \Sigma\Gamma_s c_s} \tag{1}$$

(in $\Sigma\Gamma_s c_s$, the summation extends over all components except the i-th).

From equation (1) it follows that

$$\frac{\partial a_i}{\partial c_i} = \Gamma_i \frac{1 + \Sigma\Gamma_s c_s}{(1 + \Gamma_i c_i + \Sigma\Gamma_s c_s)^2}. \tag{2}$$

From equation (2) it is seen that the presence of other components, which in development chromatography would inevitably be separated from the components of interest to us, sharply decreases the dependence of $\partial a_i/\partial c_i$ on c_i. In some cases it is advisable to add to the mixture a strongly sorbed component.

Fig. 1

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In Fig. 1 is shown an ordinary chromatogram of a mixture of iso-butane, butane, and iso-pentane on silica gel with grain size 0.25–0.30 mm ($L = 0.37$ m, $a = 1461$ cm/min, $d = 1.3$ mm), and in Fig. 1 —the vacancy chromatogram of the same mixture. The decrease in the width of the band and in the degree of asymmetry in the second case as compared with the first is evident.

Vacancy chromatography creates new possibilities with respect to the statics of sorption and ways of increasing selectivity. New ways arise for changing the nature of the sorbent, equivalent to the introduction of new types of carrier gases, stationary phases, and modifiers.

Let us note that vacant chromatography makes it possible to determine the adsorption isotherm of a mixture, which is fundamentally impossible by ordinary chromatography. Vacant chromatography opens up new possibilities for solving an important problem of modern technology—the determination of the volume of a gas sample.

In the absence of broadening, the peak area on a vacant chromatogram is directly equal to the volume of the introduced carrier gas. If the peak width is substantially greater than the initial width of the vacancy, then it does not depend on the sample volume. Therefore the peak height must increase linearly with the sample size.

Fig. 2

Figure 2 gives a calibration curve for nitrogen when using a mixture of nitrogen with butane. The use of an inertialess detector (a flame-ionization detector) makes it possible to obtain high sensitivity in determining volumes with the aid of such a chromatographic burette.

At present, in a simple version of the method it is possible to measure hundredths of a milliliter. The sensitivity can be increased by increasing the concentration of the gas (indicator) and by using other detectors.

A sharp increase in sensitivity for microchemical problems can be obtained by using, in the experiment under consideration, a moving temperature field (^{3}). The velocity vector of the field and the temperature gradients must be directed in the direction opposite to the flow velocity. In this case the band broadens and the peak height increases, which leads to an increase in the peak area and in sensitivity.

The use of vacant-chromatography methods is expedient within the framework of ordinary chromatography. Indeed, if an adsorbing indicator is introduced into the developer, then after the introduction of a sample containing n components in the carrier gas, the detector will record $n + 1$ peaks. One of the peaks will characterize the sample volume. Thanks to this, absolute calibration is substantially simplified, which is especially important for the analysis of impurities. The ratio of the areas of the components to the area of the vacancy characterizes the concentration.

It is obvious that the role of the vacancy may be played by a region with an altered concentration; therefore, the function of the dosing device may be performed by any apparatus that makes it possible to change the concentration before the column.

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

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