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Fig. 1

Figure 1: Fig. 1

Abstract

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ITERATION CHROMATOGRAPHY

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The application of gas chromatography to automatic control requires a radical change in the method itself. Expedient paths for such a change are provided by vacant chromatography (^{1}). In particular, this applies to differential chromatography (^{2}). However, in the known variants the detector is retained as an output instrument. In differential chromatography the apparatus operates according to a compensation scheme. For each component, the difference of the concentration from the nominal value is measured. But this still preserves the necessity of measuring, interpreting, or transmitting a signal for automatic control. Meanwhile it seems desirable to make the detector operate only as a null instrument, so that chromatography would always give a zero line and its recording and interpretation would lose their meaning. Such a possibility is provided by iteration chromatography, which is also one of the variants of vacant chromatography.

Fig. 1. Vacant chromatogram of mixtures of isobutane—butane (column length 1.35, diameter 0.2 cm), obtained upon introduction of a portion of air (a), butane ( ), and isobutane ( ); 1—oxygen, 2—isobutane, 3—butane. A, , —iteration steps.

Let the mixture being analyzed be passed continuously through the column. The instrument must contain a device for preparing a dose of mixture which, at certain intervals of time, is to be introduced ahead of the column into the mixture being analyzed. This dose is prepared from the carrier gas and those components of the mixture whose concentration is important for control or other purposes. In terms of the content of these components, this mixture must be close to the one being analyzed. For this purpose the device creating the dose contains elements connected with the detector.

As such elements there may be used, for example, hydraulic resistances to the flow of each component entering the mixer, from which the mixture is carried by the carrier gas into the gas being analyzed.

If the content of one of the components in the dose differs from that in the

Fig. 2

Figure 2: Fig. 2

mixture being analyzed, then at the moment the vacancy or peak arrives at the detector (depending on the sign of the concentration difference), the indication deviates from zero. This deviation, with the aid of a special device, must change the state of the indicated element (for example, the hydraulic resistance) so as to eliminate the concentration difference under consideration and ensure preservation of the zero line.

Thus, the composition of the mixture being prepared is always close to the composition of the one being analyzed. The concentration values can be read from the position-

···of the indicated elements or geometries, and the signal for regulation can be given according to the deviation of these readings from the nominal values. In the method of iteration chromatography the requirements on the range of linearity and other characteristics of the detector are reduced, since it always operates near zero readings. The ease of reading the composition and the possibility of doing without interpretation are advantages of the method. A further advantage of iteration chromatography is also the absence of the need for complete separation of the peaks, which makes this method expedient and, in a number of cases—for example, separation of isotopes—indispensable in laboratory analysis.

Fig. 2. I—Chromatogram of the separation of a mixture of hydrocarbons C_1–C_5 on a capillary column 93 m long, with an internal diameter of 0.3 mm; 1—methane, 2—ethylene, 3—ethane, 4—propylene, 5—propane, 6—isobutane, 7—isobutylene + butylene, 8—butane, 9—trans-butene, 10—cis-butene, 11—3-methylbutene-1, 12—isopentane, 13—pentene-1, 14—2-methylbutene-1, 15—isoprene, 16—pentane, 17—pentene-2, 18—2-methylbutene-2. II—Results of iteration of the isobutylene and butylene peak. A, B—iteration steps. 1, 2—mixture of isobutylene and butylene: 1—isobutylene, 2—butylene.

We carried out* iteration chromatography in two variants. In the first of them, separately prepared doses of a gas of known composition are introduced successively into the stream of the mixture being analyzed. First, pure carrier gas is introduced. Then, in the absence of separation, the blank chromatogram contains two unresolved peaks. After this, a mixture is prepared containing one of the components at a concentration corresponding to one of the two unresolved maxima of the common peak. In this case, on the blank chromatogram this component is approximately "erased," and the maximum of the resulting peak conveys the content of the second component more accurately than was the case in the primary chromatogram. The second step of the iteration (this name has been introduced by analogy with the well-known mathematical method) is the introduction of a dose with the second component at a concentration corresponding to the maximum in the peak of the first step. As a result, a more

Fig. 3. Results of iteration of mixtures: I —hydrogen—methane; II —hydrogen —methane—carbon dioxide; III —hydrogen—methane—carbon dioxide—ethylene; a, b, c, d —successive iteration steps

Figure 3: Fig. 3. Results of iteration of mixtures: I —hydrogen—methane; II —hydrogen—methane—carbon dioxide; III —hydrogen—methane—carbon dioxide—ethylene; a, b, c, d —successive iteration steps

accurate determination of the concentration of the first component is obtained. Such steps constitute a convergent process. If two successive iteration steps lead to the same concentration, then this concentration is the desired one. The complete absence of a peak upon introducing the mixture into the stream can serve as an additional check.

In the second variant of iteration analysis, the dosed mixture was prepared, as indicated at the beginning of the article, by mixing the streams of the components.

The first variant was carried out for two cases:

1. Separation of an isobutane—butane mixture on a column with Celite (60-80 mesh), impregnated with hexadecane (1% of the weight of the support). Flame-ionization detector; nitrogen carrier gas ($v = 15$ ml/min.).

* The experimental work was carried out jointly with L. A. Malyasova.

2. Separation of hydrocarbons C_1—C_5, including isobutylene-butylene, on a capillary column ($L = 93$ m, $d = 0.3$ mm) with hexadecane. Flame-ionization detector, carrier gas nitrogen ($v = 27$ ml/min.).

Figure 1 shows the result of analyzing the first mixture. Peak 1 characterizes the oxygen vacancy and is of no interest. In Fig. 1 Aa the unresolved peaks 2 and 3 represent the vacancy of the mixture of isobutane and butane. After butane was introduced into the sample in a concentration corresponding to the larger peak, peak Ab2 was obtained, approximately characterizing the concentration of isobutylene. The next peak Ab3 gives the refined concentration of butane. It is evident from Fig. 1 that the third iteration step (B) led to repetition of the butane concentration and, consequently, the iteration process proved to be completed. In Fig. 2 I the chromatogram of the second mixture is given, and in Fig. 2 II the results of iteration of the seventh peak are shown. Because of the symmetry of the peak, the concentration in the first peak corresponded to half the concentration at the maximum.

Fig. 3. Results of iteration of mixtures: I —hydrogen—methane; II —hydrogen —methane—carbon dioxide; III —hydrogen—methane—carbon dioxide—ethylene; a, , , —successive iteration steps.

The iteration is carried out more simply and rationally in another variant by applying streams of the components being introduced. The operator, by varying the rate, seeks to obtain a detector response when the sample is introduced. After this, the flowmeters directly give the composition of the analyzed mixture. We applied this method to mixtures: hydrogen–methane in nitrogen ($L = 2$ m), hydrogen–methane–carbon dioxide ($L = 1.2$ m), and hydrogen–methane–carbon dioxide–ethylene ($L = 1.0$ m). The columns were packed with Inza brick containing 35% hexadecane. The iteration results are presented in Fig. 3. Peak *a* characterizes a simple vacantochromatogram. From iteration steps , , and it is seen how easily, in three steps, the complete absence of a peak is achieved, even in the case of a four-component mixture.

These results show that the iteration method may be used as the basis not only for laboratory analysis but also for analysis carried out in production for the purpose of automatic regulation.

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CITED LITERATURE

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