

LOCATION OF THE COMPONENTS IN CHROMATOGRAMS BY MEASUREMENT OF THE THERMAL GRADIENT ARISING FROM THE HEAT OF ADSORPTION

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Measurement of the heat of adsorption of the individual components along the axis of a chromatographic column makes possible the exact location of the respective components. The measurement is accomplished by means of a micro thermocouple; the technique possesses high sensitivity and is particularly advantageous when the usual optical methods fail, *e.g.* in the case of colourless substances or a coloured adsorbent.

There exist several, well-known techniques for the detection and location of components, *e.g.* along a chromatographic column. These methods are usually based on optical observation or visualization, *e.g.* by irradiation with ultraviolet light [1, 2], of the components. Unfortunately, the principle implies the restriction that the components to be separated must be coloured or have to be visualized in some way [3—11] in order to distinguish them from each other as well as from the adsorbent itself.

We wish to report here an essentially new technique for the location of the components separated in a chromatogram. The technique is based on the known facts that migration of a component along the column consists of continuous adsorption and desorption processes, and that both adsorption and desorption processes are accompanied by thermal changes. Measurement of these, extremely minute, thermal changes, *i.e.* the thermal gradient, along the axis of the chromatographic column was found suitable for the location of the adsorbed components.

The thermal gradient was measured with the aid of a micro thermocouple (1—5 mg), simply constructed by welding together the ends of an iron and a constantan wire. It was found that the welded wires need not be isolated, as the minute voltage of a few millivolts induced by the thermal gradient was not affected by the presence of metal powders or carbon adsorbent either. The omission of the usual insulation, consisting of two ceramic tubes, considerably reduced the heat capacity of the detector and thus increased the sensitivity.

The free terminals of the thermocouple were connected either to a millivoltmeter with temperature scale or rather to a compensograph. The welded joint of the couple was then moved up and down along the axis of the column by means of an electric motor and the voltage generated in the thermocouple on passing through the adsorption zones was continuously recorded. Plotting the voltage against the position of the welded joint in the adsorbent, the exact location of the separated components in the column could be immediately obtained.

Description of the apparatus

Figure 1 shows a schematic illustration of the apparatus. The iron [2] — constantan [3] thermocouple (4) tightened by spring (7) and led by pulleys (6) is drawn up and down by electric motor (10). The movement is reversed by the device (11) as soon as the welded joint (4) has left the space filled with adsorbent. The free terminals (8) of the thermocouple are connected to compensograph (9).

A characteristic curve obtained in case of two components is also given in the figure.

Examples

a) *Examination of leaf pigments*

Dried spinach leaves were extracted with benzenemethanol (6:4) and the extract passed through a column of 20 cm height and 26 mm inner diameter filled with precipitated CaCO_3 . Subsequent to the development of the chromatogram an iron — constantan thermocouple of 0.2 mm. diameter was passed along the axis of the column with a rate of 1 cm/sec. The chromatographic column was made of a double-walled glass-tube and water of 20 °C was circulated in the jacket. In Fig. 1 both the apparatus and the temperature — displacement curve are shown, the latter in a shortened form to fit the length of the tube. A strict correlation was found between the sites of the individual components separated, as shown by their colour, and the sites of maxima observed in the compensogram.

In another experiment the adsorbent was mixed with 20(w)% black glass-powder, so that the visual evaluation of the chromatogramm was not possible. The thermal gradient, measured just as in the preceding description, indicated a decrease in the height of the maxima and simultaneously an increase in their relative distance. The adsorbent was then pushed out of the tube, cut to pieces according to the compensogram the sections were extracted with ethyl alcohol separately and each chromatographed on separate CaCO_3 columns. Each column showed then only one coloured component, proving the reliability of our method.

b) *Separation of the components of the product of a vapour-phase heterogeneous catalytic reactor*

In the course of a continuous procedure of the author (12) for the large-scale oxidative transformation of furfural to furan, *via* 2-furoic acid, it was necessary to separate the two main components of the reaction product, namely furan and carbon dioxide. This was done by adsorption on charcoal filled in a chromatographic tube, the elution being carried out by steam. The site of adsorption of furan could easily be recognized in all cases, as the heat of adsorption was so high that it could be sensed merely by hand. Application of the present technique, however, revealed the presence of another adsorption zone, namely that of carbon dioxide. Disregarding of the existence of this adsorption zone had caused serious difficulties earlier; as a matter of fact if the evaluation was started before complete removal of carbon dioxide, the latter carried along part of the furan, too, thus decreasing the yield.

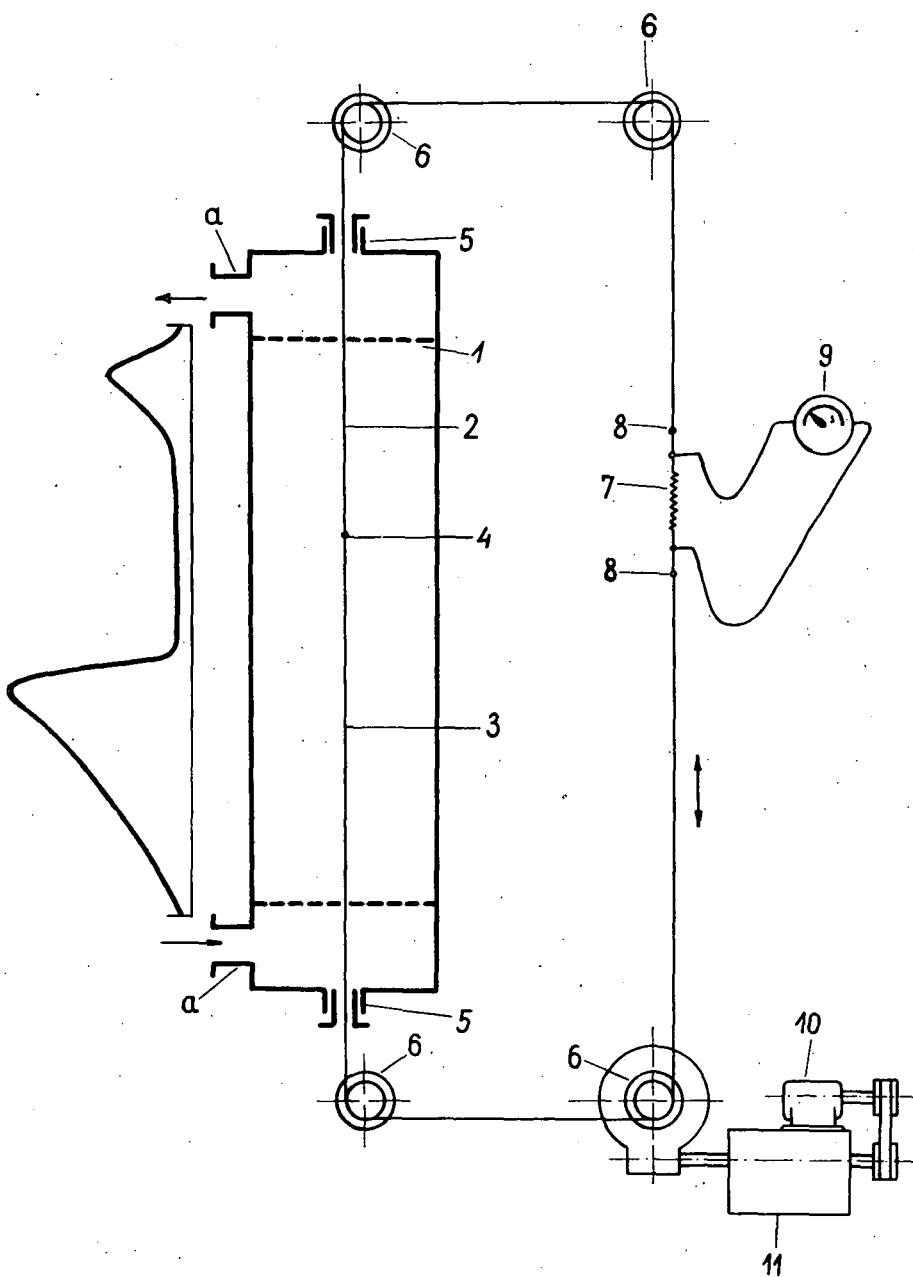


Fig. 1

Discussion

The above technique is just the reverse of that used in gas-chromatography. While in gas-chromatographs the detector is fixed and the changing medium passes through it, in our method the medium is standing (or at least almost standing) and the detector is moving. This offers wide possibilities for various technical applications both in laboratory work and in industry [13].

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УСТАНОВЛЕНИЕ МЕСТ КОМПОНЕНТОВ ХРОМАТОГРАММА ИЗМЕРЕНИЕМ ТЕМПЕРАТУРНОГО ГРАДИЕНТА ТЕПЛА АДСОРБИРОВАНИЯ

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Термоэлемент был приготовлен из железных и константановых проволок что они сварились таким образом что проволоки стали одной нитью. Проволока переходит через химические реакторы, газовой хроматограф или жидкой хроматограф с часовым механизмом и место пайки идёт по прямой линии. Включая в компенсограф, измеряется попутной тепловой градиент из которого в случае гетерогенных катализитических трубчатых печей в газовой фазе предполагается где именно химический процесс имеет место.

В случае хроматограмм определяются хроматограммы бесцветных веществ на цветных абсорбентах и потом они изолируются.

Присутствие абсорбированного фурана и углекислоты обнаружено этим методом, а десорбция фурана осуществляется после элюирования слоя углекислоты.

Термоэлемент применяя без оболочки является детектором температуры с тысячей, десятью тысячей большей тепловой инерцией.

По нашим опытам электрическое закорачивание не влияет на точность измерения.