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THE CALCULATION OF AREA FACTORS WITHOUT THE USE OF PURE COMPONENTS OF ANALYSED MIXTURES

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SUMMARY

The method of linear relationship described enables one to calculate the area factors related to a standard or to a component of an analysed mixture when the detector responds linearly to the concentration of components in the carrier gas and when mixtures with linearly independent concentrations of components are available.

INTRODUCTION

Quantitative analysis by gas chromatography of mixtures of organic compounds having different molecular weights and chemical characteristics is a complex task¹. It is difficult to obtain good resolution of all the components in the mixture and to find the area factor values which express the relationship between the component concentration in the carrier gas and the detector signal measured as the peak areas or their heights (height factor). A procedure that has been recommended is to use calibration mixtures nearly identical, qualitatively and quantitatively, to the mixture to be analysed, but this method is tedious and time consuming and cannot be applied for routine analysis, especially of mixtures that are quantitatively different. In addition, for this procedure, one must have all the components of the mixture to be analysed as chromatographically pure compounds—a difficult requirement.

The aim of this paper is to demonstrate the calculation of area factors of all the components of the analysed mixture, when no components are available as chromatographically pure compounds.

THEORETICAL

Let us make the following assumptions: (1) The detector signal measured as the peak area (or peak height) is proportional to the concentration of the component. (2) The quantities of the samples injected into the column are chosen so that concentrations of all the components remain within the linear region of the detector. (3) A

stock of m mixtures of unknown quantitative composition is available, and it contains at least as many mixtures with a linearly independent concentration as there are components, n , in the analysed mixtures. Thus m must be greater than or equal to n . By this method, the qualitative composition can be unknown, peaks being designated by numbers. (4) All components are shown as peaks on the chromatogram and no component is adsorbed in the column.

Procedure 1

A definite amount (by weight, volume or other unit of measure) of the standard which must be chromatographically pure and whose peak must not interfere with those of the components is added to each stock solution. From the chromatogram of the mixture analysed with standard the data for the following equation is obtained.

$$k_s P_s + \sum_{i=1}^n k_i P_i = Q + Q_s \quad (1)$$

where k is the area factor of the standard s or the component i ; P is the peak area of the standard s or the component i ; $Q = \sum_{i=1}^n Q_i$ is the corrected area of all components; $Q_s = k_s P_s$ is the corrected area of the standard. Because

$$\frac{Q}{Q_s} = \frac{C}{C_s} \quad (2)$$

eqn. 1 can be written in the form

$$\sum_{i=1}^n \frac{k_i}{k_s} \cdot P_i = \frac{C}{C_s} \cdot P_s \quad (3)$$

where

C is the weight of the sample analysed, and

C_s is the weight of standard added.

For each mixture we obtain eqn. 3 and a set of such equations can be solved by the conventional method when $m = n$ or by the least-squares procedure when $m > n$. When calculated in that way, the area factors k_i/k_s are used for calculating appropriate percentage concentrations, X , of all components in each mixture analysed, using the formula

$$X_i = \frac{\frac{k_i}{k_s} \cdot P_i}{\sum_{i=1}^n \frac{k_i}{k_s} \cdot P_i} \cdot 100 \quad (4)$$

Procedure 2

Any component in the mixture analysed, denoted by k , which is available in a chromatographically pure state can be used as a standard. In this case from the chromatogram of the analysed mixture, we have

$$\sum_{i=1}^n k_i P_i = Q \quad (5)$$

and from the chromatogram of a mixture with a definite amount of component k we obtain the equation

$$\sum_{i=1}^n k_i P_i' = Q$$

The area of the peak of component k , P_{kk}' , must be related to the amount of the analysed mixture, from which the first chromatogram was obtained. This is calculated by

$$P_{kk} = P_{kk}' \frac{\sum_{\substack{i=1 \\ i \neq k}}^n P_i}{\sum_{\substack{i=1 \\ i \neq k}}^n P_i'} \quad (6)$$

Then the following equation is true:

$$\sum_{\substack{i=1 \\ i \neq k}}^n k_i P_i + k_k P_{kk} = Q + Q_{kk} - Q_k \quad (7)$$

Because

$$Q_{kk} - Q_k = k_k (P_{kk} - P_k) \quad (8)$$

and

$$\frac{Q}{Q_{kk} - Q_k} = \frac{C}{C_{kk}} \quad (9)$$

then

$$\sum_{\substack{i=1 \\ i \neq k}}^n \frac{k_i}{k_k} \cdot P_i = \frac{C}{C_{kk}} (P_{kk} - P_k) - P_k \quad (10)$$

where C_{kk} is the weight of component k added.

Taking $k_k = 1$, a set of equations such as eqn. 10 enables one to calculate the area factors k_i by a conventional or least-squares procedure. The percentage concentrations of all components can be calculated from the formula

$$X_i = \frac{k_i P_i}{\sum_{i=1}^n k_i P_i} \cdot 100 \quad (11)$$

Procedure 3

This procedure is the simplest one but only can be applied if strictly the same amount of analysed mixture (e.g. by volume) is injected into the chromatograph. Then the area factors can be calculated from a set of equations in the following form.

$$\sum_{i=1}^n k_i P_i = 1 \quad (12)$$

The percentage concentration of all components can be calculated from eqn. 11. The percentage concentrations are related, of course, to appropriate units of measure (weight, volume, etc.)

DISCUSSION

It is obvious that the results obtained by these procedures will be more accurate if the conditions for analysis satisfy the above assumptions. Accuracy can be judged statistically by estimating pure error and lack of fit². If the lack of fit is significant, there are two situations possible. Firstly, one or more components, whose concentrations are not constant in all the mixtures, are adsorbed in the column. Secondly, the assumption that the detector signal is a linear function of the concentration of the component is false. Then the relation between concentration or corrected area and the area recorded by the detector may be better expressed by the formula

$$Q_1 = k_1 P_1 + k_{11} P_1^2 \quad (13)$$

In the second case, good results can be obtained by procedure 1 if (a) the standard can be added in quantities that remain in the linear range of the detector or (b) if constant amounts of standard are added to all the mixtures and if their peaks have identical or nearly the same areas.

Then the following equation holds.

$$\sum_{i=1}^n \left(\frac{k_1}{k_s} P_1 + \frac{k_{11}}{k_s} P_1^2 \right) = \frac{C}{C_s} P_s \quad (14)$$

To calculate k_1/k_s and k_{11}/k_s , an appropriate stock of analysed mixtures, containing at least n mixtures with linear independent concentrations, should be available. Others mixtures can be produced by combining two other mixtures.

The percentage concentrations of all the components can be calculated from the equation

$$X_1 = \frac{\frac{k_1}{k_s} P_1 + \frac{k_{11}}{k_s} P_1^2}{\sum_{i=1}^n \left(\frac{k_1}{k_s} P_1 + \frac{k_{11}}{k_s} P_1^2 \right)} \cdot 100 \quad (15)$$

Requirement b that has been given above is practically the same as that for procedure 3—that identical amounts of each sample must be injected into the chromatograph. Area factors can be calculated from the set of equations

$$\sum_{i=1}^n (k_1 P_1 + k_{11} P_1^2) = 1 \quad (16)$$

The percentage concentrations are calculated from an equation similar to eqn. 15.

All procedures that have been discussed require a stock of mixtures with linearly independent concentrations. If the concentration of any component slightly differs throughout the stock or if the concentrations of the components in different mixtures are almost linearly dependent, it is advantageous to have at least one or more chroma-

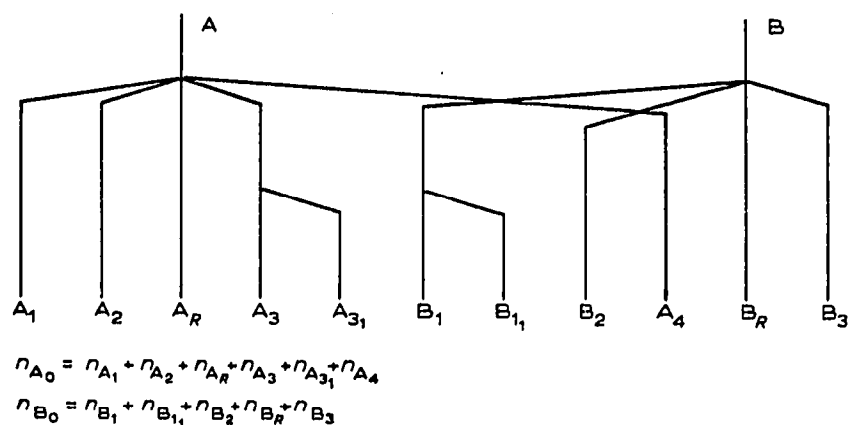


Fig. 1. The spectra of products of substances A_0 and B_0 .

tographically pure components or to have only components of the analysed mixtures as impurities. These components can be mixed with analysed mixtures to make their concentrations more linearly independent.

The number of mixtures needed for calculation of area factors can be reduced if we can accept some assumptions concerning some components and create conditions which characterise their sums. This may be explained, for example, by quantitative analysis of a mixture which contains products and residues after having undergone chemical reaction, *e.g.* over a catalyst (Fig. 1).

As substances A and B do not yield the same products (the spectra of their products are independent), the sum of the products and residues of A in moles equals the number of moles of A present in the starting mixture; the same is true for B. In this way, the molar area factors are separately calculated for products and residues of A and B, and the required number of analysed mixtures with linearly independent concentrations of components may be reduced from 11 to 5.

Such an approach to the quantitative analysis of mixtures enables one, firstly, to reduce the number of mixtures needed for calculating area factors and the number of unknowns in sets of equations, and, secondly, to check some assumptions concerning the reaction mechanism.

Using the computer for calculation of area factors and of concentration of components and using at least the necessary number of analysed mixtures, the area factors and concentration of components may be estimated with higher accuracy for each consecutive analysed mixture.

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