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APPLICATION OF THE "ISOTHERMAL RELATIVE CONCENTRATION METHOD" IN GAS CHROMATOGRAPHY

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SUMMARY

A method is proposed in which a sample is introduced into a chromatograph through a sorbent-filled sample tube, total pre-saturation of the sorbent with the mixture to be analyzed and desorption in the carrier gas stream being effected at the same constant temperature. This method enables one to determine the relative concentrations of the components. Possible applications are discussed.

INTRODUCTION

In trace analysis, a concentration step is often a vital phase of gas chromatographic procedures. In general, by concentration the so-called absolute concentration is meant, which results in an increase in the absolute concentration of the constituent being determined compared with its level in the mixture being analyzed. However, in certain instances discussed below, it is expedient to effect a selective increase in the amount of the component introduced into the chromatograph without varying its concentration. Thus, the amount of this component increases with respect to some other component adopted as a standard, *i.e.*, so-called "relative concentration" takes place.

In order to determine relative concentrations, it is proposed to employ a method¹, tentatively called the "isothermal relative concentration method". In this method, the sample tube is a U-shaped sorbent-filled tube, which is first purged with the mixture being analyzed until saturation, then coupled into the gas chromatograph system in a standard manner before the chromatographic column, and purged with carrier gas at the saturation temperature. In order to saturate the sorbent in the sample tube, the volume of the mixture being analyzed which passes through it must be sufficiently large to establish equilibrium between the gas phase and the sorbent for the heaviest component throughout the entire sorbent layer.

This method is, to some extent, similar to the absolute concentration method developed by Janák and co-workers^{2,3}, which also involves pre-saturation of the sorbent in the sample tube; however, the difference lies in the isothermal conditions of sorbent saturation and sample discharge employed.

The relative concentration approach is a simple method enabling one to introduce into the chromatograph samples large enough to obtain a stepped chromato-

gram^{4,5}. Stepped chromatography has a number of advantages, such as improved signal stability and detection sensitivity, direct proportionality of the step height to the concentration of the sample being analyzed, which simplifies quantitative interpretation, and elimination of errors due to partial irreversible adsorption of the trace components on the apparatus and the sorbent.

THEORETICAL

The amount of the i th component, Q_i , introduced with the use of an empty sample tube of volume V_0 is

$$Q_i = c_i V_0 \quad (1)$$

where c_i is the concentration of the i th component. Then, the amount of the i th component introduced with the help of the same sample volume filled with a sorbent, Q'_i , is (neglecting the pressure drop)

$$Q'_i = c_i V_{Ri}^0 = c_i (V_{Ni} + V_d) \quad (2)$$

where V_{Ri}^0 is the retention volume of the i th component for a sample tube filled with a sorbent, V_{Ni} is the net retention volume of the i th component, and V_d is the dead volume of a sorbent-filled tube.

It is reasonable to express the efficiency of this method in terms of the relative concentration. This value is determined from eqn. 3, which indicates the factor by which the amount of the i th component varies relative to the amount of the standard component:

$$\frac{\beta}{\alpha} = \frac{V_{Ri}^0}{V_{Rst}^0} \quad (3)$$

where

$$\alpha = \frac{Q_i}{Q_{st}} = \frac{c_i}{c_{st}} \quad (4)$$

$$\beta = \frac{Q'_i}{Q'_{st}} = \frac{c_i}{c_{st}} \cdot \frac{V_{Ri}^0}{V_{Rst}^0} \quad (5)$$

and c_{st} , Q_{st} and Q'_{st} , and V_{Rst}^0 , are the concentration, amounts and retention volume of the standard component, respectively. If the standard is a non-sorbed component, *i.e.*, $V_{Rst}^0 = V_d$, then, for practical purposes, the relative concentration coincides with the extraction factor, K :

$$\frac{\beta}{\alpha} = \frac{V_{Ri}^0}{V_d} \approx \frac{KV_s}{V_d} \quad (6)$$

where $V_s = (V_0 - V_d)$ is the sorbent volume, and K is the distribution coefficient.

EXPERIMENTAL AND RESULTS

Some examples illustrating the features of the proposed technique are considered below.

Fig. 1 shows the results of analysis of sulphur dioxide (0.117%) and water admixtures (0.07%) in nitrogen by the conventional and proposed methods. Water and sulphur dioxide were separated in a column (1 m × 4 mm I.D.) filled with Polysorb-1 (which has adsorption properties similar to those of Porapak Q) at 60°. The peaks in Fig. 1a were obtained with the sample introduced by use of an empty gas sample tube of $V_0 = 5$ ml. The steps in Fig. 1b were obtained with the sample introduced by use of the same sample tube but filled with Polysorb-1 and pre-saturated with the mixture to be analyzed; saturation and desorption of the sorbent were carried out at 18°.

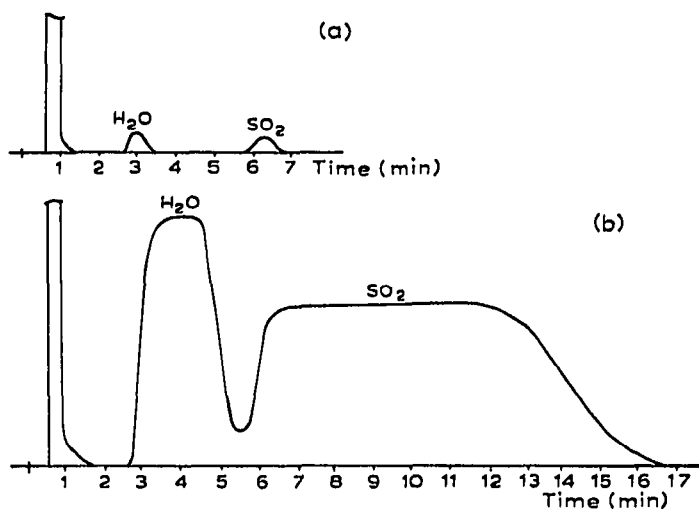


Fig. 1. Determination of water and sulphur dioxide in nitrogen. (a) Conventional chromatogram; (b) chromatogram obtained by the relative isothermal concentration method.

As a result of the stepped chromatogram, the signal heights were 40 times higher for water and 53 times higher for sulphur dioxide. The relative concentrations of sulphur dioxide and water relative to the non-sorbed gas (nitrogen) were

$$\frac{V_{RSO_2}^0}{V_d} = \frac{574}{4.4} = 130; \quad \frac{V_{RH_2O}^0}{V_d} = \frac{143}{4.4} = 32.5$$

The amount of the heavier component, sulphur dioxide, introduced with the sample increased more than 4-fold compared with the lighter component, water.

Similar results were obtained for carbon dioxide (0.014%) and hydrogen sulphide (0.09%) in nitrogen (Fig. 2). The separation of the components was effected in a column (0.7 m × 4 mm I.D.) filled with silica gel at 100°. The gas sample tube was also filled with silica gel in order to obtain a stepped chromatogram. Saturation

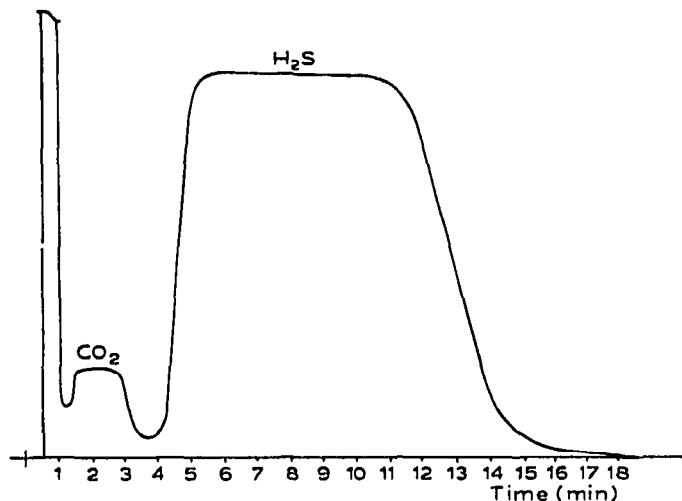


Fig. 2. Stepped chromatogram of carbon dioxide and hydrogen sulphide.

and desorption were carried at 22°. The relative concentrations of the components relative to nitrogen were

$$\frac{V_{RH_2S}^0}{V_d} = \frac{400}{5} = 80; \quad \frac{V_{RCO_2}^0}{V_d} = \frac{100}{5} = 20$$

The signal heights increased by 18 times for hydrogen sulphide and 1.7 times for carbon dioxide. It should be mentioned that the values calculated by eqn. 3 agreed with the values calculated by the ratio of the step areas of the components.

The relative concentration method was also employed in order to obtain stepped chromatograms for acetone and carbon disulphide (Fig. 3). In this experiment, a separation column (2 m × 4 mm I.D.) was filled with Chromosorb W coated with 15% polyethylene glycol 300, and a sample column filled with Celite coated with 15% dinonyl phthalate was saturated with the mixture to be analyzed and purged at 20°.

The important advantages of the proposed method are the smaller size of the

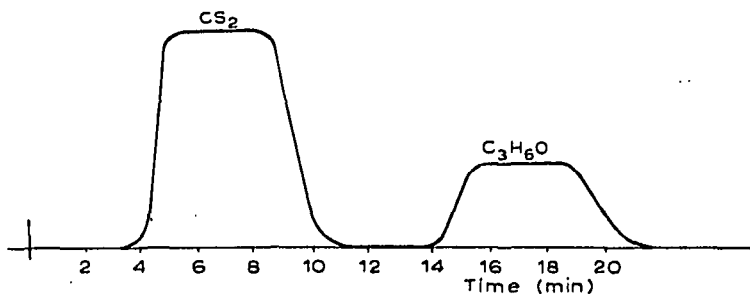


Fig. 3. Stepped chromatogram of carbon disulphide and acetone.

apparatus and the insignificant intermixing with the introduction of large samples. Introduction of large samples by the conventional method using calibrated volumes involves great difficulties stemming from intermixing and disturbances of the hydrodynamic conditions of the system, which limits the application of stepped chromatography. Thus, for instance, we failed to obtain stepped chromatograms of sulphur dioxide and water by the conventional method.

CONCLUSION

The above features of the isothermal relative concentration method as a means for the introduction of large samples, in our opinion, show its suitability for a wide range of applications. It should be possible to use it in stepped chromatography, preparative chromatography, the analysis of trace amounts of substances, particularly of aggressive substances and heavy admixtures with subsequent temperature programming of the separating column, and the analysis of gases at reduced pressure. The method should also have similar applications in liquid chromatography.

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