Notes

Direct measurement of column hold-up in gas–liquid chromatography when using ionization detectors

To determine the absolute retention data the "gas hold-up"[1] in gas–liquid chromatography (GLC) must be evaluated. When using detectors which respond to permanent gases the gas hold-up can be directly measured from the air peak corresponding to the elution of a non-absorbed air sample. Since ionization detectors are insensitive to permanent gases the direct "air peak" method is not applicable under the conditions prevailing in a conventional GLC apparatus. Therefore, several indirect methods[2–7] have been proposed based on the linear relationship of the logarithm of the corrected retention time and the carbon number of a homologous series[8]. Using this linear relationship the gas hold-up has been evaluated as a "mathematical air peak"[2,3] and as a "calculated dead time[4–7] from the retention times of at least three members of a homologous series. The only direct method reported in the literature is that of "methane peak", which is considered unreliable as a generally applicable method[7,9] because of the small solubility of methane in organic solvents.

During the present work it has been found that when the carrier gas is presaturated with a low volatility organic solvent, negative air peaks can be readily detected with a hydrogen flame ionization detector. By measuring the retention time of the air peak and making allowance for the vapour pressure of the solvent, the gas hold-up of the apparatus can be directly determined. The gas hold-up of a packed column was directly determined by the above air peak method. Fig. 1 shows the injection points, the negative air peaks and the *n*-butane peaks for three identical vapour samples of *n*-butane–air mixture as detected with a hydrogen flame ionization detector. The carrier gas was presaturated with the solvent (*n*-decane) at the column temperature of 30.0°.

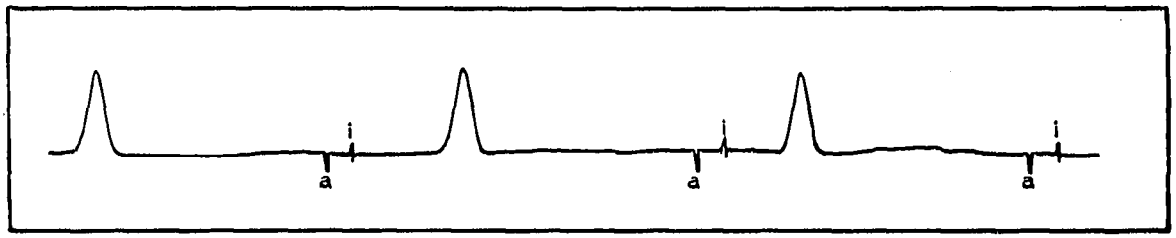

Fig. 1. Chromatogram of *n*-butane–air samples on *n*-decane showing injection points (i) and air peaks (a). Each sample is a 1.0 ml mixture containing 3.6×10^{-4} g *n*-butane.

The gas hold-up determined from the above method was compared with that estimated from a method recommended for capillary columns[1] and based on calculating the interstitial volume from the column characteristics. The method was modified for calculating the gas hold-up in the packed column in such a way that the

combined volume of the column, the sample injector and the detector was determined before packing the column by measuring the volume corresponding to the peak maximum of an organic solute in the dry nitrogen carrier gas and with no solvent or solid support in the column. The volume of the solvent was determined by an internal standard. The volume of the solid support was calculated from its density as determined by a specific gravity bottle. The results from the two methods differ by 2 %. The difference was mainly due to uncertainty in the effective volume of the solid support.

It is concluded that with hydrogen flame ionization detector it is now possible to determine directly, by air peak, the gas hold-up of GLC apparatus by presaturating the carrier gas with an organic solvent prior to the injection of the air sample. In the case of non-volatile solvents, the carrier gas may be saturated with any other suitable organic solvent of low volatility at the column temperature.

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Resolution of amino acids by gas chromatography*

The resolution of racemic mixtures of secondary *n*-alkanols by gas chromatography of the corresponding diastereoisomeric α-hydroxypropionates has been reported earlier[1,2]. The present communication describes a similar approach to the separation of α-amino acids.

The amino acids examined were chromatographed in the form of N-trifluoroacetyl (N-TFA) esters[3] of 2-*n*-alkanols, the latter serving to introduce an additional asymmetric center. The derivatives were prepared in nearly quantitative yields by esterification in the presence of HCl, and treating the resulting amino ester hydrochlorides in methylene chloride solution with excess trifluoroacetic anhydride at —20° with stirring. The reaction mixture was allowed to warm up to room temperature and left for 1 h.

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