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Deactivation of the gas chromatographic support for the separation of aliphatic amines

The main difficulty encountered in the gas–liquid chromatographic separation of the aliphatic amines is caused by the adsorption of the latter compounds to the quasi-inert chromatographic support[1]. The adsorption effect, when fairly weak, leads to the formation of asymmetric peaks, making impossible the proper quantitative evaluation of the separated compounds. In a less favorable case when the adsorption is very strong, no elution of the chromatographed compounds occurs. Probably the most disadvantageous situation may be found in the analysis of mixtures containing minor concentrations of strongly adsorbed compounds. It may happen that such compounds will be retained in the column, thus escaping identification[2,3].

Various methods have been proposed to suppress or diminish adsorption of the compounds to be chromatographed on the inert support. However, it is impossible to review them all in this note—only a short account on that subject is given here. Thus, generally speaking, these methods are concerned either with the deactivation of the support by alkali treatment[4,5] or with the application of high-boiling organic bases[2,6,7] (including detergent powders[8,9]) as liquid phases. The application of poly(tetrafluoroethylene) molding powder as the inert support[10] or the saturation of the carrier gas with an amine[11] have also been proposed.

In the present note a very simple and convenient method of deactivation of the inert support prior to its proper impregnation with a liquid phase suitable for resolving the primary and secondary aliphatic amines is described. This method consists in treating the inert support (such as Chromosorb P or W) with sodium metanilate(3-aminobenzene-1-sulphonate). Metanilic acid, unlike the other aminobenzenesulphonic acids, is thermally and chemically stable (it is very resistant, for instance, to desul-

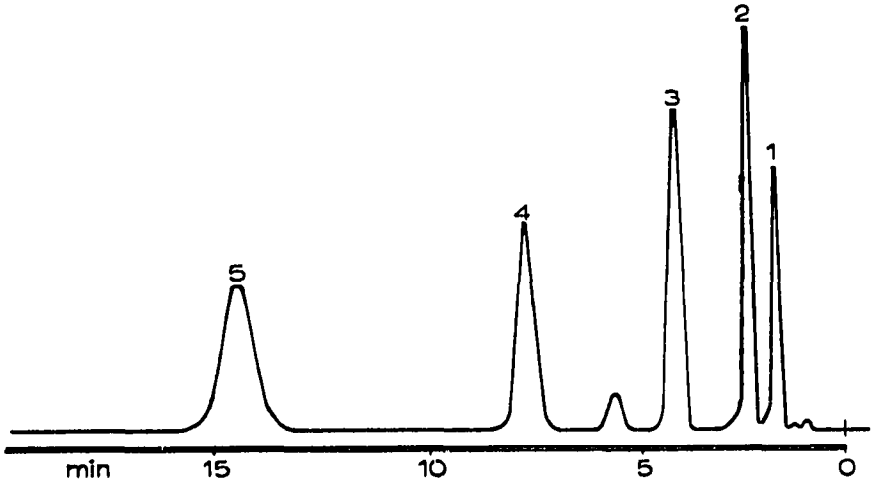

Fig. 1. The resolution of C_2–C_4 aliphatic secondary amines. 1 = diethylamine; 2 = diisopropylamine; 3 = di-*n*-propylamine; 4 = diisobutylamine; 5 = di-*n*-butylamine. Apparatus: Perkin-Elmer gas chromatograph, Model 452, equipped with a hot-wire detector, stainless-steel column (200 × 0.4 cm) filled with Apiezon L (10%) on deactivated Chromosorb W, 60/80 mesh; temperature, 104°; carrier gas hydrogen (40 c.c./min); sample size, 1 μl.

phonation[12]). It was considered that sodium metanilate would block the active sites of the support and consequently suppress the adsorption of the amino groups.

An example will illustrate the method: an appropriate amount of the inert support was treated with 5% (calculated on the support) sodium metanilate in methanol (the latter should totally cover the support), the solvent consequently evaporated to dryness. The support so pretreated was in turn impregnated with Apiezon L or any other liquid phase, the only limitation being that the solvent used for impregnation should not dissolve sodium metanilate. With such a pretreated support, the following column fillings were prepared: Apiezon L (10%), Carbowax 5000 (10%) and Reoplex 400 (10%), all on Chromosorb P and W. All these fillings were investigated for resolution of aliphatic primary and secondary amines at temperatures up to 160°. The column containing Apiezon L was used even at 180° for several weeks without any deterioration of its efficiency. A typical separation of low-boiling aliphatic secondary amines on Apiezon L is shown in Fig. 1, with the experimental details given in the legend. Quite satisfactory results as to the shape of peaks were obtained on columns containing Carbowax 5000 and Reoplex 400. However, the resolution of the analysed amines on the polar liquid phases, especially on Reoplex 400, was less interesting due to the superimposition of some peaks.

The analyses of pyridine bases (picolines and some lutidines) were also effected on the Apiezon L and Reoplex 400 columns with satisfactory results.

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