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Short Communication

Immobilized polyethyleneglycol-based stationary phase for the analysis of amines and organic acids by capillary gas chromatography

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ABSTRACT

A procedure for preparing capillary columns for the analysis of amines and organic acids with a working temperature of 55–300°C was developed for a column coated with immobilized Carbowax 20M/SE-54 stationary phase mixture. The inner wall of the capillary was deactivated with 3-aminopropyl triethoxysilane.

INTRODUCTION

Capillary columns and currently used stationary phases do not enable successful simultaneous analysis of substances of acidic and basic character. In practice, however, such an analysis is required.

The analysis of free fatty acids and other substances —alcohols or phenols containing an active hydroxyl group in their molecule— is limited to the use of capillary columns containing a stationary phase prepared specially for separation of acids. Most frequently polar stationary phases of the polyethyleneglycol type modified with organic acids, such as terephthalic acid or its derivatives, are used [1–3].

Basic heterocyclic nitrogenous compounds and aromatic and aliphatic amines can be separated on various stationary phases, *e.g.* polyethylenimine, polypropylenimine or polyethyleneglycol, with the addition of potassium hydroxide [4], or on some polysiloxane stationary phases [3]. For the analysis of amines, capillary columns with a non-immobilized stationary phase of polyethyleneglycol-type Carbowax 51 have been specially prepared and are commercially available. Recently CP WAX has been used for the analysis of diamines and volatile amines [5]. For the analysis of N-nitroso substances, aromatic and heterocyclic amines and other amino substances, Carbowax Amine capillary columns have been recommended [6].

The requirement for simultaneous analysis of acidic [7] and basic substances could eventually be met by a capillary column containing a mixture of phases.

This work is concentrated on the preparation of capillary columns containing an immobilized film of a mixed stationary phase of poly-

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ethyleneglycol/polysiloxane type with sufficient thermostability suitable for the analysis of acidic and basic solutes. The preparation of the columns was based on knowledge derived from, and modified procedures of, preparation of polyethyleneglycol-type immobilized stationary phase based on polyurethane [8] and polysiloxane-type stationary phase immobilized by a radical mechanism known commercially as SE-54 [9]. Some chromatographic properties of this stationary phase were studied.

EXPERIMENTAL

Chemicals and materials

Simax glass tubes were obtained from Kavalier (Sázava, Czech Republic). Capillary columns containing immobilized and non-immobilized Carbowax 20M (the glass capillary inner surface silanized with a 5% solution of γ-glycidoxypropyltrimethoxysilane [8]) and an immobilized SE-54 silicone stationary phase film (the inner surface silanized with $[^2H_4]$octamethylcyclotetrasiloxane [9]) were prepared in the Institute of Analytical Chemistry, Czech Academy of Sciences, Brno, Czech Republic.

Most of the chemicals were supplied by Lachema (Brno, Czech Republic). The following chemicals were obtained: 3-aminopropyl triethoxysilane (Serva Feinbiochemica, Heidelberg, Germany), $[^2H_4]$octamethylcyclotetrasiloxane (VCHZ Synthesia, Kolín, Czech Republic), Carbowax 20M (Carlo Erba, Milan, Italy), SE-54 silicone stationary phase (W. Günter, Düsseldorf, Germany), azo-*tert.*-butane (Ventron, Karlsruhe, Germany), Desmodur L 75 (Bayer, Dormagen, Germany) and DABCO R-8020 (Air Products Group, Paulsboro, NJ, USA).

Apparatus

The device for drawing glass capillaries was manufactured in the Institute of Analytical Chemistry, Czech Academy of Sciences, Brno, Czech Republic. The capillary columns were thermostated and tested in a Fractovap Model 2300 AC gas chromatograph equipped with a flame ionization detector (Carlo Erba, Milan, Italy).

Preparation of the capillary column containing the mixed stationary phase

Glass capillaries (0.25 mm I.D.) made of Simax glass were drawn by the usual procedure [10]. The inner capillary surface was silylized with 5% 3-aminopropyl triethoxysilane in methanol. Capillaries filled to the 85–90% level with a solution of silane were heated in a thermostat at 80°C for 2 h. Then they were washed with 2 ml of methanol and blown with nitrogen for 30–60 min.

The capillary tubes deactivated by silylation were further coated with the mixed stationary phase from its dichloromethane solution [0.6% (w/v) Carbowax 20M and 0.05% (w/v) SE-54], according to the static method. The solution also contained Desmodur L 75 ($2 \cdot 10^{-3} M$) and DABCO R-8020 catalyst ($5 \cdot 10^{-5} M$).

In the first step Carbowax 20M was cross-linked by heating the sealed column at 145°C for 5 h. Nitrogen was blown through the column. The prepared columns (10–15 m × 0.25 mm I.D., film thickness 0.4 μm) were first tested at 110°C with 2,6-dimethylphenol and 2,6-dimethylaniline to determine efficiency and capacity factor. Nitrogen was used as the carrier gas at the velocity of 10–11 cm/s.

In the second step the column was blown with a stream of nitrogen saturated at 25°C with azo-*tert.*-butane for 1 h (for SE-54 cross-linking) at a flow-rate of 2 cm/s. The sealed column was heated in a thermostat from 40 to 220°C at 10°C/min and then left at 220°C for 1 h. After three cycles, it was washed with 2 ml of chloroform at a rate of 1 cm/s and blown with nitrogen

TABLE I

PROPERTIES OF THE IMMOBILIZED CARBOWAX 20M/SE-54 STATIONARY PHASE MIXTURE

Degree of cross-linking (%)	Column efficiency (theoretical plates/m)	
	2,6-Dimethylphenol	2,6-Dimethylaniline
89.6	5000	4800

Fig. 1. Chromatogram of volatile free fatty acids. Glass capillary column: 10 m × 0.25 mm I.D.; film thickness: 0.4 μm; stationary phase: immobilized Carbowax 20M/SE-54 mixture; column temperature: 130°C; carrier gas: nitrogen; velocity: 10 cm/s. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = isobutyric acid; 4 = *n*-butyric acid; 5 = valeric acid; 6 = caproic acid.

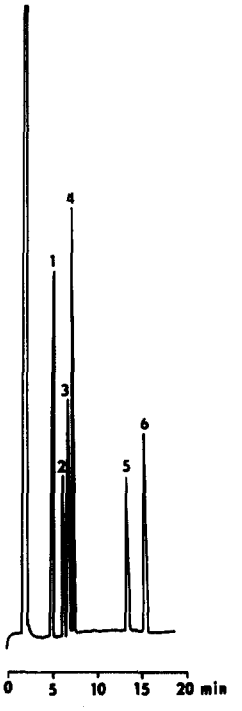

Fig. 2. Chromatogram of heterocyclic and primary amines. Column as in Fig. 1; column temperature programmed from 70 to 100°C at 2°C/min; carrier gas: nitrogen; velocity: 10 cm/s. Peaks: 1 = butylamine; 2 = pyridine; 3 = propylamine; 4 = 4-methylpyridine; 5 = hexylamine; 6 = 4-ethylpyridine.

for 1 h. The procedure was then repeated with 2 ml of methanol and the columns retested.

The degree of stationary phase film immobilization in the treated columns was calculated as the ratio of the capacity factor of 2,6-dimethylphenol after washing the column to that of the same solute before washing, expressed as a percentage.

TABLE II

RETENTION INDEX VALUES OF SELECTED SUBSTANCES MEASURED ON COLUMNS CONTAINING NON-IMMOBILIZED CARBOWAX 20M, IMMOBILIZED CARBOWAX 20M, SE-54 AND CARBOWAX 20M/SE-54 MIXTURE STATIONARY PHASES, AT 60°C

Test substance	I_R			
	Non-immobilized Carbowax 20M	Immobilized Carbowax 20M	SE-54	Carbonwax 20M/ SE-54 mixture
Benzene	955	987	688	902
1-Butanol	961	1228	679	1106
1,4-Dioxane	1073	1173	714	1017
Pyridine	1187	1366	753	1121

RESULTS AND DISCUSSION

Some properties of the capillary columns prepared are summarized in Table I. As an example of application of this stationary phase, a mixture of lower fatty acids (Fig. 1) and a mixture of heterocyclic and primary amines (Fig. 2) are shown.

Influence of immobilization on the polarity of a stationary phase mixture

The influence on polarity of the immobilization procedure used was studied by means of retention indices (I_R) of the test substances determined on columns coated with the non-immobilized and immobilized Carbowax 20M stationary phase films, the immobilized stationary phases mixture film (Carbowax 20M/SE-54) and the immobilized SE-54 stationary phase film. The results in Table II show that the retention indices for all substances on the capillary column coated with the immobilized Carbowax 20M/SE-54 mixture were lower than on the capillary column containing immobilized Carbowax 20M. The retention index values obtained show that the immobilized Carbowax 20M/SE-54 mixed stationary phase is less polar than immobilized Carbowax 20M and that the stationary phase film is mildly acidic.

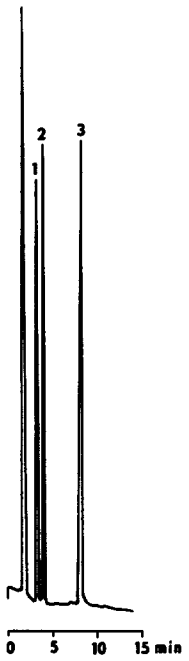

Fig. 3. Chromatogram of solutes mixture. Column as in Fig. 1; column temperature: 270°C; carrier gas: nitrogen; velocity: 10 cm/s. Peaks: 1 = pentachlorphenol; 2 = 2,2-bipyridyl; 3 = acridine.

Temperature stability of the immobilized stationary phase mixture film

The working temperature interval for the immobilized Carbowax 20M/SE-54 stationary phase mixture is in the range 55–300°C. In such a column a mixture of solutes at 270°C was chromatographed (Fig. 3).

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