

GROUND UNGLAZED TILE—A NEW SUPPORT FOR
GAS-LIQUID CHROMATOGRAPHY** **

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The preparative separation of the terpene components of essential oils by means of gas-liquid chromatography¹ requires supports of higher qualities than separation for analytical purposes. The material must have great permeability since the separation is carried out in columns of considerable length. Since some terpenes are unstable at higher temperatures, the separation must be performed under mild conditions, *i.e.* under reduced pressure. The choice of the rate of flow of the carrier gas is thus limited by the maximum inlet pressure permissible. One strict requirement is complete chemical inertness of the support. This condition must be observed very closely, particularly in the separation of terpenes sensitive to the catalytic action of metallic ions or those that at elevated temperatures may be affected by the acidic or basic nature of the support itself. Finally, an important feature is the mechanical resistance of the support towards abrasion since dust formed in any of the operations results in irregular streaming of the carrier gas and causes an increase of the pressure gradient in the column and this adversely affects the elution of individual components.

These requirements are not met by any of the common supports such as celite¹, sterchamol² or kieselguhr^{3***}.

This was already observed by NAVES⁴, who also found the customary supports unsuitable for the separation of essential oils. He suggested using classified sea-sand or sodium chloride as inert support. We have now found that finely ground unglazed white tile is an inert support of high quality.

EXPERIMENTAL AND RESULTS

Preparation of the support

Unglazed tile ("Rako")† was crushed in a ring-roller mill, screened on sieves to the grain size of 0.2–0.3 mm, decanted with water to remove the dust, dried and ignited at 300°.

* Czechoslovak patent application for the use of unglazed tile as a support is pending (PV 6264/58).

** Presented at the 6th Meeting of workers in the field of Gas Chromatography, Gottwaldov, June 1959.

*** Celite (C-545, Johns Manville, London); sterchamol (Sterchamolwerke, Dortmund); kieselguhr SK (Calofrig, Borovany near České Budějovice).

† Ceramic Works of Rakovník (National enterprise), Rakovník.

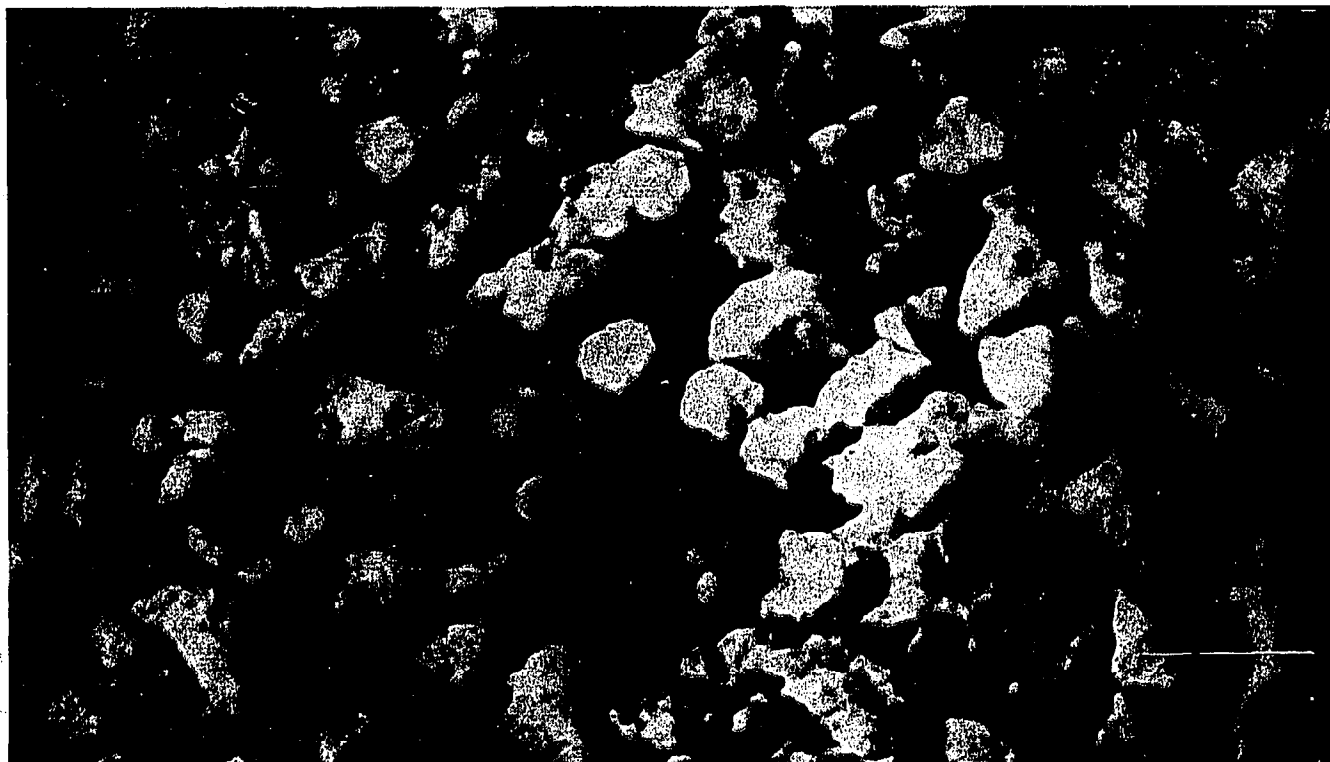


Fig. 1. Microphotograph of the tile support, magnified 30 times.

The support prepared in the manner described is a white material which is mechanically very resistant in comparison with sterchamol or kieselguhr. The individual particles have an irregular shape (Fig. 1). The surface of a fraction with a particle size of 0.2–0.3 mm, measured by the BET⁵ method, is 2.2 m²/g.

This tile support was wetted with an ethereal solution of tricresyl phosphate so that the concentration of tricresyl phosphate was 5 %, 7 %, 10 %, 13 % and 18 %, respectively.

Efficiency of the support

To compare the efficiency of this support with that of sterchamol, a simple artificial mixture of monoterpene hydrocarbons (α -pinene, myrcene, Δ^3 -carene, limonene, and *p*-cymene) was chromatographed, under identical conditions, on sterchamol wetted

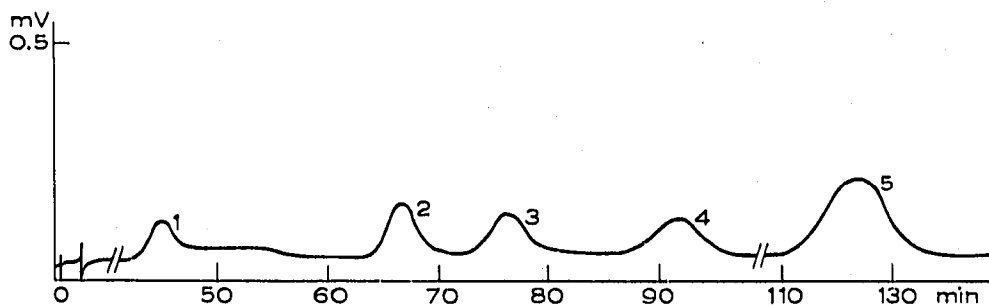


Fig. 2. Chromatogram of a mixture of monoterpene hydrocarbons: (1) α -pinene; (2) myrcene; (3) Δ^3 -carene; (4) limonene; (5) *p*-cymene. Support: sterchamol; stationary phase: tricresyl phosphate (20 %); temperature: 138°; column length: 240 cm; rate of flow: 19.7 ml N₂/min.

with 20% tricresyl phosphate⁶ (Fig. 2), and on the tile support containing varying amounts of the stationary phase. As can be seen from Fig. 3, optimum separation was obtained by using a support containing 7% of the stationary phase. Column efficiency is expressed as number of theoretical plates⁷ for Δ^3 -carene. Column resolution was calculated for myrcene and Δ^3 -carene by methods recommended in the literature^{8,9}.

In order to determine whether the tile support catalyses chemical reactions of the compounds being chromatographed, as is the case with kieselguhr, the following

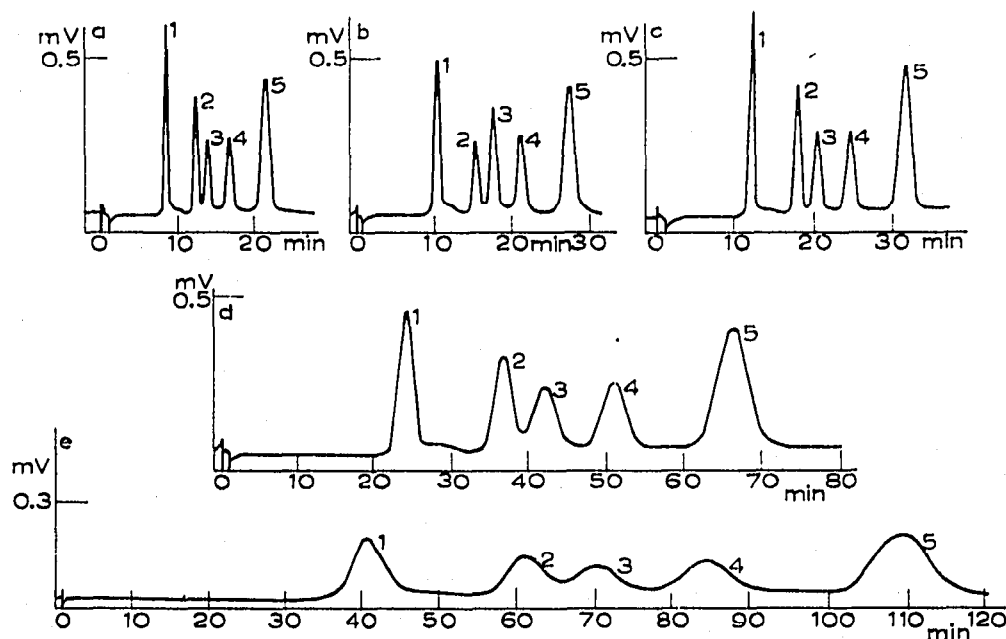


Fig. 3. Comparison of the separation of a mixture of monoterpene hydrocarbons (the same as in Fig. 2) with various concentrations of tricresyl phosphate on the tile support. Temperature: 136° ; column length: 240 cm; rate of flow: 19.7 ml N_2 /min. (a) 5%, (b) 7%, (c) 10%, (d) 13% and (e) 18% of stationary phase.

experiment was carried out: 2 ml of pure α -pinene was boiled, the vapours were passed through a 5 cm thick layer of tile support heated electrically to 150 – 160° , and then condensed by a reflux condenser. Three comparative experiments were carried out using unglazed tile, sterchamol and kieselguhr support, respectively. Neither sterchamol nor the tile support caused any noticeable chemical change, whereas kieselguhr produced some β -pinene as judged by infra-red spectroscopy of the starting and recovered material.

Apparatus and experimental conditions

All measurements were carried out with the analytical apparatus of Griffin and George (London), type IIA, using a conventional set-up containing a thermal conductivity platinum detector and a millivoltmeter-recorder with the range 0–1 mV. The carrier gas was nitrogen, the temperature of the air-thermostat 136° and the length of the chromatographic column 240 cm.

The preparative separation was carried out with an improvised apparatus, which

will be described later. This apparatus had a column of 4.5 m by 17 mm and was capable of separating 0.7 g of a mixture of terpene hydrocarbons.

DISCUSSION

As compared with currently used supports, the tile support has a considerably greater mechanical resistance. It resists abrasion and does not form fine dust. This property is especially advantageous in the case of long columns, where the permeability is adversely affected by the dust formed from kieselguhr or sterchamol.

The surface of the tile support is less by an order of magnitude than that of sterchamol or kieselguhr, but this does not seem to be prohibitive to its use, as can be seen from Fig. 3a-e. The small surface of the tile support and also the smaller volume of the pores merely lowers the maximum content of the stationary phase. However, the maximum wetting of the tile support, *i.e.* 18 wt.% based on the weight of the support is not optimal for the separation of the terpene hydrocarbons, the most convenient concentration being 7-10% (Fig. 3b,c). In this case the same resolution as on the sterchamol column can be achieved (see Table I). A great advantage of the

TABLE I

Support	Tricresyl phosphate %	TP* for Δ^3 -carene	Column resolution**		Pressure in column, mm Hg	
			A	B	inlet	outlet
Ground unglazed tile	5	1536	1.25	0.58	446	193
	7	2270	1.41	0.94	401	207
	10	1025	1.12	0.82	670	455
	13	868	0.98	0.73	416	210
	18	712	0.88	0.64	671	359
Sterchamol	20	1745	1.53	0.93	671	621

* Calculated by the method recommended by the Committee⁷ of the 1st Symposium on Vapour Phase Chromatography, London, 1956.

** A: Calculated by the method recommended by the Committee⁸ of the 2nd Symposium on Gas Chromatography, Amsterdam, 1958. B: Calculated by the method of STRUPPE⁹.

tile support is further its chemical inertness to unsaturated compounds as was shown by the experiment with α -pinene described in the experimental part.

The high mechanical resistance allows an easy recovery of the tile support by extraction of the stationary phase and ignition of the dried material. The tile support has the further advantage of easy availability, simple recovery and low cost.

In addition to the analysis and preparation of monoterpene hydrocarbons, this support proved to be suitable for the analytical separation of other mixtures such as monoterpene alcohols, monoterpene ketones, esters of dicarboxylic acids¹⁰, stereoisomers of cyclic alcohols¹¹, etc.

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SUMMARY

A new support for gas-liquid chromatography made of crushed unglazed white tiles is described. Its surface is 2.2 m²/g, the maximum wettability is 18% for tricresyl phosphate, the optimum amount of the stationary phase for the separation of monoterpene hydrocarbons being 7-10%. This support has no catalytic effects on terpene hydrocarbons, is mechanically very resistant, allows relatively high flow rates, and is easy to recover. Its function was experimentally compared with that of sterchamol using a mixture of monoterpene hydrocarbons.

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