

## Note

### New detection method for compounds with a labile halogen on thin-layer chromatograms

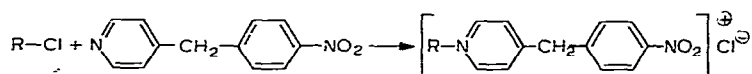
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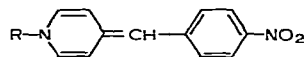
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The detection and identification of some industrially important products, compounds containing a reactive halogen atom, can be carried out by paper or thin-layer chromatography. The spots of negatively charged benzene derivatives, such as *o*- and *p*-chloronitrobenzenes, chloro-2,4-dinitrobenzenes and picryl chloride, can be visualized by the characteristic fluorescence quenching of the nitro compounds or by the colour reaction with the Ehrlich reagent following reduction by stannous chloride in hydrochloric acid<sup>1,2</sup>. Under such conditions the compound is detected by means of other characteristic groups. Organic halogen acids can be visualized by the acid-base method: aromatic halogen acids by use of the reaction with hydroxylamine and a cupric salt<sup>3</sup>, alkyl halogenes by use of the reaction with silver nitrate<sup>4</sup>.

The above reactions cannot be used for the detection of halogenated heterocyclic compounds such as cyanuric chloride, 2-alkoxy-4,6-dichloro-*s*-triazine, 2,4,6-trichloropyrimidine, 2,4,5,6-tetrachloropyrimidine and 2,3-dichloroquinoxaline. These compounds<sup>5</sup> can be detected using the colour reaction with 4-(*p*-nitrobenzyl)pyridine, as described for the determination of yperite<sup>6</sup> and for the detection of methyl bromide<sup>7</sup> and phosgene in air<sup>8</sup>, where after the loss of the labile halogen a coloured salt is formed:



A deepening of the colour<sup>7</sup> can be achieved in an alkaline medium<sup>9</sup> or in the presence of piperidine<sup>7</sup>:



## EXPERIMENTAL

Silufol plates (15 × 15 cm) (Glass Works Kavalier, Votice, Czechoslovakia) were used. The development took place in a chromatographic chamber (18 × 8 × 17

cm). The standard solutions for the chromatography were prepared by dissolving of 50 mg of sample in 2 ml of benzene-acetone (1:1). The detection agents were prepared: by dissolving of 1 g of 4-(*p*-nitrobenzyl)pyridine (Lachema, Brno, Czechoslovakia) in 250 ml of 96% ethanol (a); by stirring of 50 ml of this solution with 5 ml of piperidine (b).

#### *Thin-layer chromatography*

Aliquots of 2  $\mu$ l of the standard solutions were applied 2 cm from the edge of the Silufol plate using a micropipette. After evaporation of the solvent, the development was carried out by the ascending method using the solvents benzene ( $S_1$ ) and benzene-heptane (1:1) ( $S_2$ ) at the room temperature of 22–23°. When the solvent front had travelled 10 cm from the start, the development was interrupted and the solvent was allowed to evaporate. The chromatogram was then sprayed with the ethanolic solution of 4-(*p*-nitrobenzyl)pyridine and the coloration was developed on warming in a stream of hot air (55–65°).

#### RESULTS AND DISCUSSION

The results of the chromatographic separation and the colours of the spots are summarized in the Table I.

TABLE I

$R_F$  VALUES AND COLOURS OF THE SPOTS OF COMPOUNDS CONTAINING LABILE HALOGEN

Compound	$R_F$		Colour after detection with	
	$S_1$	$S_2$	$a^*$	$b^*$
Chloro-2,4-dinitrobenzene	0.74	0.32	yellow	yellow
Fluoro-2,4-dinitrobenzene	0.66	0.22	violet	black
Picryl chloride	0.76	0.26	gray-black	black
Benzyl bromide	0.90	0.79	violet	violet
2,4-Dinitrobenzyl bromide	0.68	0.19	—	violet-ochre
Cyanuric chloride	0.78	0.50	red	red-carmine
4,6-Dichloro-2-methoxy-1,3,5-triazine	0.49	0.20	red	red
2,4,6-Trichloropyrimidine	0.81	0.55	red	red
2,4,5,6-Tetrachloropyrimidine	0.86	0.66	red	red
2,3-Dichloroquinoxaline	0.87	0.54	violet	yellow
Phosphonitrile chloride	0.95	0.93	orange	red-orange

\* For a and b, see under Experimental.

The formation of the coloration after the detection confirms the course of the suggested reaction at the compounds containing labile halogen. The greater the reactivity of the halogen and its readiness to nucleophilic attack, the more easy is the course of the reaction. This is evident especially in the cases of picryl chloride (chloro-2,4,6-trinitrobenzene), fluoro-2,4-dinitrobenzene and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) where is not necessary to warm the chromatogram after spraying. The reaction does not proceed for compounds in which the carbon-

halogen bond exhibits aromatic character, and where the carbon atom is not sufficiently activated. This was confirmed for *o*- and *p*-chloronitrobenzene, benzyl chloride and 1,4-dichlorophthalazine. The more reactive benzyl bromide gave a positive test. The coloration of the spots is stable for several days, the detection limit for cyanuric chloride being 0.5–1.0  $\mu\text{g}$ .

Chromatographic separation in combination with the described method of the detection can be used to advantage for the determination of the purity of cyanuric chloride or for the elucidation of the course of its alkoxylation.

#### ACKNOWLEDGEMENTS

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