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Note

Qualitative and quantitative determination of *m*-toluidine and its alkyl derivatives by gas–liquid chromatography on free fatty acid phases*

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N-Ethyl-*m*-toluidine (MEMT) (b.p. 221°C) and N,N-diethyl-*m*-toluidine (DEMT) (b.p. 231°C) are commercially important intermediates for dyes and photographic chemicals. For example, 2-amino-5-diethylaminotoluene hydrochloride is used as a photographic colour developer. Ethylation of *m*-toluidine gives MEMT and DEMT, and a rapid and efficient method was necessary to detect and determine the presence of one in the other and in the presence of *m*-toluidine. Pasechnik and Rogovik[1] separated the three components by gas–liquid chromatography (GLC) using a KhL-6 chromatograph equipped with a thermal conductivity detector and a 180 cm × 6 mm I.D. column packed with polymethylphenylsiloxane-4 (25% of the weight of the carrier) coated on Chromosorb W (60–80 mesh). The carrier gas was helium, the flow-rate was 60–65 ml/min, the column temperature was maintained at 170°C and the time of emergence of all the components in the mixture containing *m*-toluidine, MEMT and DEMT was 30 min. However, there was no mention of the elution pattern or of their retention times.

The objective of this investigation was to find a column that would give a rapid and efficient separation and also eliminate the need for higher loadings and consequently higher column temperatures. A column of 10% FFAP (free fatty acid phases; Carbowax 20M terminated with 2-nitroterephthalic acid) coated on 2% potassium hydroxide-treated Chromosorb W AW DMCS was suitable and gave a baseline separation of MEMT, DEMT and *m*-toluidine.

EXPERIMENTAL

Materials and solvents

MEMT and DEMT were distilled twice before use. *m*-Toluidine (Fluka) was used as received.

For the analysis of technical DEMT, aniline was selected as an internal standard. The aniline was freshly distilled before use.

Methanol was dried and then distilled before use.

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Instrumentation

A Hewlett-Packard (HP) Model 700 gas chromatograph equipped with a dual flame ionization detector was used, together with an HP 3380A integrator and an HP 240 temperature programmer. The following conditions were used: detector temperature, 300°C; injection port temperature, 40°C above the oven temperature; oven temperature, 140–150°C; carrier gas flow-rate, 40 ml/min; and chart speed, 0.5 cm/min.

Stationary phase

A seamless aluminium column (1.8 m × 4 mm I.D.) was filled[2] with 10% FFAP coated on Chromosorb W AW DMCS (60–80 mesh), treated with 2% potassium hydroxide solution. Conditioning[3] was carried out at 220°C overnight.

Preparation of the standard and the unknown mixtures

Standards of different compositions ranging from 0.1 to 0.5% were prepared in methanol while keeping the weight of the internal standard constant (10 mg in 10 ml). Similarly unknown mixtures were prepared with the same amount (10 mg) of internal standard added.

For quantitative analysis, 2 μl of the standard and unknown solutions were injected.

RESULTS AND DISCUSSION

The analysis was initially carried out on the following columns: (1) 10% FFAP on 2% potassium hydroxide-treated Chromosorb W AW DMCS; (2) 10% FFAP on non-silanized Chromosorb W; (3) 10% Carbowax 20M on 2% potassium hydroxide-treated Chromosorb W AW DMCS; and (4) 10% Carbowax 20M on 2% potassium hydroxide-treated non-silanized Chromosorb W. It was found that an efficient separation of MEMT and *m*-toluidine could not be achieved on Carbowax 20M on either potassium hydroxide-treated non-silanized or potassium hydroxide-treated silanized supports (3 and 4). Further, the retention times were longer and the peaks broader. The time required for the analysis was about 10 min longer than when FFAP was used as the stationary phase. The separation of MEMT and *m*-toluidine was efficient on column 1 than on column 2. Hence column 1 was chosen for the separation and analysis of the toluidine derivatives.

Baseline separation of all the components was possible when the qualitative analysis was carried out at 150°C; Fig. 1 shows the chromatogram obtained at 150°C. Aniline was used as the Internal standard. The total time of emergence of all the components was 14.22 min (Table I). The detector response factors of the samples are expressed relative to the internal standard[4]. By keeping the amount of internal standard constant, it was possible to obtain calibration graphs without actually determining the relative response factors by plotting the peak-area ratio (R_A) against percentage composition on weight ratio (R_Q).

In order to reduce the systematic errors in the analysis, the R_A *vs.* R_Q graphs could be constructed for a definite concentration (10 mg per 10 ml) of the standard and for a definite injection volume (2 μl)[5]. The results obtained after injecting the unknown synthetic mixture are given in Table II. A technical sample of DEMT

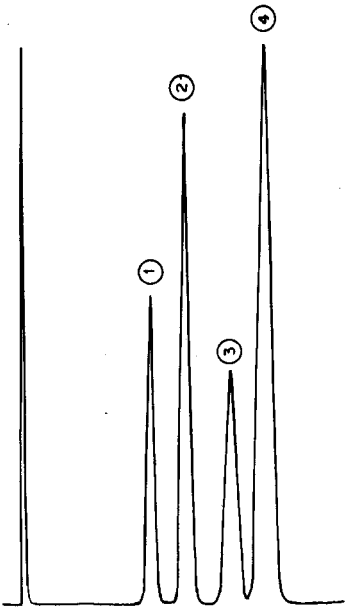

Fig. 1. Quantitative analysis of alkyl-substituted *m*-toluidines after addition of aniline as an internal standard. Peaks: 1 = DEMT; 2 = aniline; 3 = MEMT; 4 = *m*-toluidine.

TABLE I

RETENTION TIMES OF THE COMPONENTS DURING QUALITATIVE AND QUANTITATIVE ANALYSIS

Sample No.	*Temperature (°C)*	*Retention time (min)*			
		DEMT	*MEMT*	*m-Toluidine*	*Aniline*
1*	140	11.32	17.58	20.06	–
2**	150	8.06	12.39	14.22	9.85

* Qualitative analysis.
** Quantitative analysis.

TABLE II

DETERMINATION OF *m*-TOLUIDINE AND ITS N-ALKYL-SUBSTITUTED DERIVATIVES ON A 10% FFAP COLUMN AT 150°C

Sample	*Weight (mg)*		*Composition (%)*		*Error (%)*		*Standard deviation* of the peak area ratio*
	Actual	*Exptl. (graph)*	*Actual*	*Exptl. (graph)*	*Weight*	*Composition (%)*	
DEMT	21.9	22.0	0.219	0.220	−0.45	−0.45	$2.8 \cdot 10^{-2}$
MEMT	24.0	24.0	0.240	0.239	0.00	+0.41	$7.8 \cdot 10^{-2}$
m-Toluidine	63.2	63.0	0.632	0.630	+0.31	+0.31	$6.4 \cdot 10^{-2}$

* Number of determinations = 6.

containing MEMT as an impurity was injected and its peak area-ratio was determined. By plotting this value on the calibrated graph the weight ratio (R_Q) could be found:

$$R_Q = \frac{\text{weight of sample}}{\text{weight of standard}}$$

From this simple equation the actual weight (in mg) of MEMT was calculated (Table III). The standard deviations for the unknown synthetic mixture and for the technical sample were calculated and are given in Tables II and III, respectively.

TABLE III

RESULTS OBTAINED FROM GRAPH AFTER INJECTING A TECHNICAL SAMPLE

Peak-area ratio	*Composition (%) (graph)*	*Weight ratio, R_Q (graph)*	*Weight (mg)*	*Standard deviation* of the peak area ratio*
1.50	0.13	1.33	13.7	$9.3 \cdot 10^{-2}$

* Number of determinations = 6.

CONCLUSION

The chromatograms obtained show that the column used here is more efficient and provides faster separations than that used by Pasechnik and Rogovik[1]. The precision of the method is high, as can be seen from standard deviations for the unknown synthetic mixture and for the technical sample. This method can be used for the quality control of commercial DEMT and MEMT.

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