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Note

Gas chromatographic retention indices of tear gases on capillary columns

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Tear gas compounds (lacrimators) cause irritation of the eyes, nose, respiratory tract and skin with the consequent production of profuse tears and mucous. On prolonged exposure individuals may suffer acute pain in the chest, difficulty in breathing and vomiting[1]. Methods are required for their rapid and sensitive identification, and gas chromatography (GC) with a fused-silica capillary column is the method of choice due to its high resolution power and sensitivity.

The correlation of retention indices between an unknown and reference compound on two or more columns of different polarities is generally sufficient for identification purposes. The measurement of Kováts retention indices[2] is useful only when compounds with similar retention behaviour are to be studied, as the column temperature in these measurements is held constant. Recently, temperature-programmed retention indices using Van den Dool and Kratz equation[3] have been found to be useful for compounds of defence interest[4–7].

In this paper we report temperature-programmed retention indices for several tear gas compounds using Van den Dool's equation[3]. GC of these compounds as a class on a fused-silica capillary column and temperature-programmed retention indices for most of them have not previously been reported. Further, the measurement of retention indices on two columns with different polarities is shown to be applicable for the identification of tear gases in air.

EXPERIMENTAL

Standards

C_6–C_8 *n*-alkanes were purchased from BDH (Poole, U.K.) and C_9–C_{24} *n*-alkanes from Fluka (Buchs, Switzerland).

Tear gas compounds

Chloroacetone (A-Stoff) was obtained from Fluka and methyl ethyl ketone, benzyl chloride, benzyl bromide, ethyl cyanoacetate, benzoyl chloride and ethyl bromoacetate from BDH.

ω-Chloroacetophenone (CN) was prepared by chlorination of acetophenone[8]. *o*-Chlorobenzylidene malononitrile (CS) was prepared by condensation of *o*-chlorobenzaldehyde with malononitrile[9].

The purity of all the compounds was checked by GC before further use and was found to be >99% in all instances. Further, CS and CN were characterized by IR and MS data (CS, $M^{+\cdot}$ = m/z 188; CN, $M^{+}_{\bullet}$ = m/z 154.) Their melting points were in good agreements with literature values.

Instrumentation

A Shimadzu Model GC-9APTF gas chromatograph equipped with a flame ionization detector and a Chromatopak C-R3A data processor was used. Two fused-silica capillary columns (30 m × 0.32 mm I.D.) with a 0.25-μm film of surface-bonded and cross-linked stationary phase were used: (a) DB-1701 (86% dimethyl-, 14% cyanopropylphenyl polysiloxane) and (b) DB-1 (100% dimethylpolysiloxane), supplied by J & W Scientific (Folsom, CA, U.S.A.). The carrier gas was nitrogen at 1.25 kg/cm^2 at the inlet. Hydrogen was supplied to the detector at 40 ml/min and air at 400 ml/min. The column oven temperature was held at 60°C for 2 min, increased at 8°C/min up to 200°C. The injector block was kept at 210°C and the detector block at 230°C. A splitless Grob-type injection system was used.

Measurement of retention indices

In order to measure the retention indices, generally solutions containing several tear gases in acetone together with *n*-alkane standards were injected on to the GC column. The sample size in each instance was about 0.1 μl. The amounts of individual tear gases and *n*-alkanes present were in the range 10–15 ng. The retention times were recorded with an accuracy of up to 0.001 min with the help of the Shimadzu C-R3A data processor.

In order to identify individual components in the mixture, an authentic sample of each tear gas was injected separately and its retention time was compared with that of the component in mixture.

Temperature-programmed retention indices for individual compounds were calculated as described in literature[3].

RESULTS AND DISCUSSION

Temperature-programmed retention indices for tear gas compounds on two capillary columns are given in Table I. The reliability of the retention indices depends on the accurate measurements of retention times and reproducible temperature programming and carrier gas flow-rates. The retention times were measured in up to 0.001-min increments. The reproduciblity of the temperature programming was satisfactory. The flow-rate of the carrier gas and other chromatographic conditions were maintained constant. The standard deviation of the retention index of any particular compound was less than 0.8 (n = 5).

Errors arising from deterioration of the stationary phase can be avoided by use of bonded phases. Application of a small sample size (0.1 μl) with nanogram level concentrations of the components helped in avoiding errors that generally arise from overloading of the column. The peaks were sharp and symmetrical even on polar phase. A typical chromatogram for some tear gas compounds obtained on the DB-1701 column is shown in Fig. 1.

As can be seen from the data in Table I, the retention indices on the polar

TABLE I

TEMPERATURE-PROGRAMMED RETENTION INDICES OF TEAR GAS COMPOUNDS ON DB-1 AND DB-1701 FUSED-SILICA CAPILLARY COLUMNS

Heating rate 8°C/min. Other GC conditions as described in the text.

Compound	*Retention index*[a]		
	DB-1	*DB-1701*	ΔI
Methyl ethyl ketone	721.6 ± 0.3	810.6 ± 0.2	89.0
Chloroacetone	850.6 ± 0.6	989.8 ± 0.4	139.2
Bromoacetone	876.5 ± 0.5	1027.6 ± 0.4	151.1
Ethyl bromoacetate	986.5 ± 0.5	1061.5 ± 0.6	75.0
Benzyl chloride	1002.2 ± 0.5	1122.5 ± 0.4	120.3
Ethyl cyanoacetate	1026.7 ± 0.4	1140.8 ± 0.4	114.1
Benzoyl chloride	1038.5 ± 0.6	1193.7 ± 0.7	155.2
ω-Chloroacetophenone (CN)	1229.8 ± 0.5	1471.7 ± 0.8	241.9
o-Chlorobenzylidene malononitrile (CS)	1487.6 ± 0.5	1810.4 ± 0.5	322.8

[a] Mean ± S.D. ($n = 5$).

stationary phase are higher than those on the non-polar phase. Further, the difference in the retention indices value on the polar and non-polar columns (ΔI) is higher for aromatic compounds such as CS and CN than for aliphatic compounds such as bromoacetone. The large variations in the ΔI values can be attributed to the different chemical natures and physical properties of the tear gases studied.

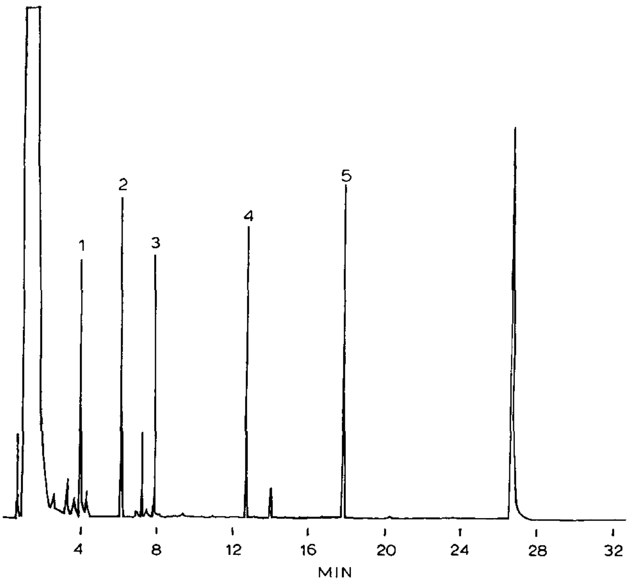

Fig. 1. Separation of tear gases on a DB-1701 fused-silica capillary column (30 m × 0.32 mm I.D., film thickness 25 μm). Chromatographic conditions are described in the text. Peaks: 1 = chloroacetophenone; 2 = benzyl chloride; 3 = benzoyl chloride; 4 = CN; 5 = CS.

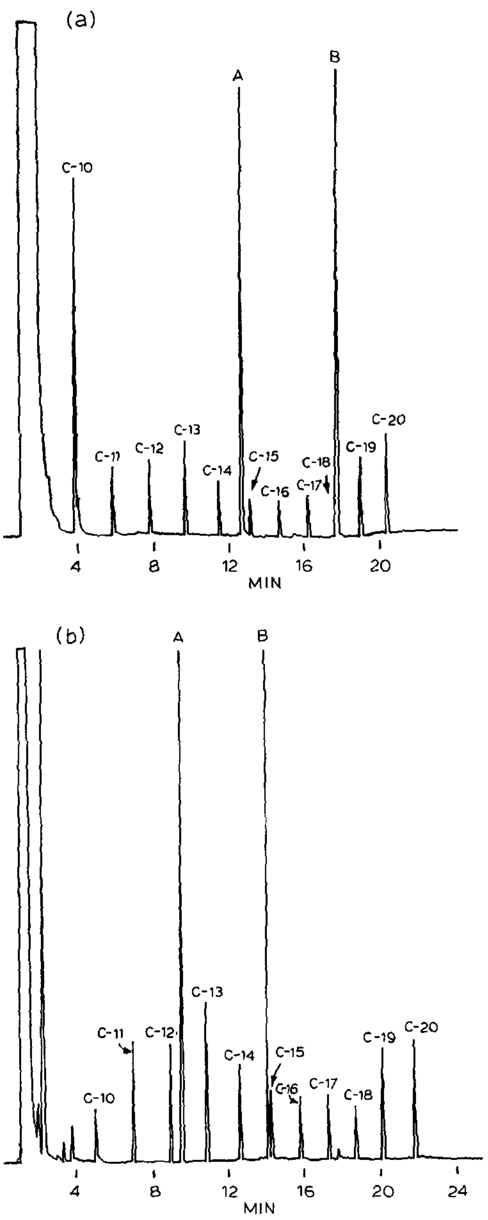

Fig. 2. Chromatograms obtained on (a) DB-1701 and (b) DB-1 columns for tear gas compounds recovered from a contaminated air sample. Peaks: A = CN; B = CS; C-10 to C-20 = *n*-alkanes.

The retention indices for CN and CS obtained here are in very good agreement with those reported by D'Agostino and Provost[4]. However, data for other compounds was not available in the literature.

TABLE II

RETENTION INDICES FOR CN AND CS RECOVERED FROM CONTAMINATED AIR IN COMPARISON WITH EXPECTED VALUES

GC conditions as described in the text.

Peak	*Retention index*[a]			
	DB-1		*DB-1701*	
	Observed	*Expected*[b]	*Observed*	*Expected*[b]
A (CN)	1226.5 ± 0.6	1229.8 ± 0.5	1470.8 ± 0.5	1471.7 ± 0.8
B[c] (CS)	1485.2 ± 0.7	1487.6 ± 0.5	1807.2 ± 0.6	1810.4 ± 0.5

[a] Mean ± S.D. (n = 5).

[b] See Table I.

[c] See Fig. 2.

Analysis of artificially contaminated air samples

To check the applicability of method for the identification of tear gas compounds in air, air in a closed container was artificially contaminated with vapours of CN and CS. It was then passed through a cold acetone trap (0°C) and the trap solution was subjected to GC analysis together with *n*-alkane standards. Typical chromatograms obtained on the two columns for CN and CS after recovery from air are shown in Fig. 2. Table II shows the observed and expected retention indices for these compounds, which are in good agreement.

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