Retention index monitoring of compounds of chemical defence interest using thermal desorption gas chromatography

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(First received June 19th, 1990; revised manuscript received October 3rd, 1990)

ABSTRACT

Retention index monitoring using thermal desorption gas chromatographic analysis was developed as a method for the verification of compounds of chemical defence interest in environmental matrices. Gas chromatography retention indices were determined by loading solid adsorbent packed sampling tubes initially with the target compounds and subsequently with a series of *n*-alkane probes. The resulting chromatographic performance and gas chromatography retention indices were shown to be independent of the tube loading method. A database of gas chromatography retention indices for chemical warfare agents and simulants was compiled and, in conjunction with simultaneous flame ionization and flame photometric detection, applied to the identification of triethyl phosphate, tributyl phosphate and diethyl malonate in water and soil samples.

INTRODUCTION

Sampling tubes packed with solid adsorbents are routinely used to sample organic compounds from a variety of matrices [1–7]. Analyte vapour, drawn through the sampling tube and concentrated by selective adsorption, may then be desorbed from the adsorbent by one of two methods: (i) thermal desorption, where the compounds are volatilized and swept from the adsorbent or (ii) solvent desorption where the analytes are extracted with a suitable solvent. When coupled to a gas chromatograph, thermal desorption offers greater sensitivity as all the analyte, on the adsorbent, may be introduced directly onto the column for analysis. Thermal desorption gas chromatographic (TD–GC) techniques typically only allow one analysis per tube, making it necessary to maximize the information from each GC analysis. GC retention index monitoring coupled with single or multiple detectors is an effective method for the tentative identification of analytes, when the retention index of the analyte has been determined prior to analysis. While this method is an effective

screening procedure, confirmation of the identity of a detected analyte must be based on a technique like gas chromatography–mass spectrometry.

Standardization of GC retention information by determining retention indices relative to a homologous series of chemical probes was first proposed by Kováts in 1958 [8]. Samples are typically spiked with a mixture of probes (usually a series of n-alkanes) and the retention index for the component of interest calculated relative to the retention times of the neighbouring probes. This technique, initially designed for isothermal analysis, was subsequently refined for temperature programming, thus enabling the analysis of compounds of varying volatility in a single analysis [9]. Temperature programmed GC retention indices were calculated using Van den Dool's equation:

$$I_c = 100n \left[\frac{t_{R(c)} - t_{R(z)}}{t_{R(z+n)} - t_{R(z)}} \right] + 100z$$

where: c is the compound of interest, n is the difference in carbon number between the two n-akanes either side of the compound of interest, t_R is the retention time, z is the carbon number of the n-alkane immediately prior to compound c, and I_c is the GC retention index of compound c.

GC retention information in the form of GC retention indices have been reviewed recently [10,11] and databases for numerous classes of chemical compounds have been published. Generally GC retention indices for compounds of defence interest have been reported relative to n-alkanes [12–15] and recently relative to a series of alkyl bis(trifluoromethyl)phosphine sulphides [16,17]. Although given consideration as a technique for chemical warfare (CW) verification [18], application of retention indices during thermal desorption gas chromatography appears to be unique. The Defence Research Establishment Suffield (DRES) has developed the Minitube Air Sampling System (MASS), an integrated sampling and analysis system based on miniature solid adsorbent packed sampling tubes (minitubes) and TD–GC analysis [19]. This paper reports the use of GC retention index monitoring in conjunction with TD–GC for the analysis of compounds of chemical defence interest found on schedule [1] of the Annex to Article VI of the developing United Nations Chemical Weapons Convention (CWC). A database of GC retention indices of CW agents as well as some common simulants was created using four fused silica capillary columns of varying polarity. Application of TD–GC retention index monitoring in a verification role for the identification of analytes by headspace and purge and trap techniques was demonstrated using spiked environmental samples.

EXPERIMENTAL

Materials

Minitubes were constructed of borosilicate glass tubes 38 mm × 2 mm I.D. and packed with 15 mg of Tenax TA (Chrompack, Blenheim, Canada). A standard solution of n-alkane probes (200 ng/μl each), C_7–C_{20} and C_{22}–C_{32} (even numbers only), was prepared from individual standards (Alltech, Deerfield, IL, U.S.A.) in glass distilled hexane (BDH, Toronto, Canada).

The chemical warfare agents, their degradation products and methyl salicylate

were obtained from the DRES Organic Chemistry Laboratory. Dimethyl sulphoxide, diethyl malonate and glass-distilled acetone were purchased from BDH. Triethyl phosphate and tributyl phosphate were obtained from Fisher Scientific (Fair Lawn, NJ, U.S.A.).

Sample handling

A vapourizing unit was constructed from a GC injection port that had been modified to allow external temperature control and insertion of a minitube. The minitube was positioned at the outlet of the injector in order to minimize heat transfer to the tube during loading. Target compounds and retention index probes were injected into the vapourizing unit with a 10-μl syringe. A one minute transfer time from the injector to minitube, at a nitrogen flow rate of 75 ml/min, was used for each sample.

Air sampling was performed in a sealed plexiglass vapour chamber approximately 0.75 m^3 in volume. A 5-μl volume of the compound to be analyzed was placed in a heated glass dish and allowed to vapourize for 3 min while the air in the chamber was circulated using an electric fan. Air was then drawn through the minitube for 1.5 min at 50 ml/min. The retention index probes were subsequently loaded on the minitube using the vapourizing unit described above.

A 2-ml water sample spiked with 20 μg/ml triethyl phosphate was purged with nitrogen (75 ml/min) for 30 min and the volatilized analytes were trapped on a minitube. *N*-Alkane probes were then added and the minitube analyzed by TD–GC with simultaneous flame ionization (FID)–flame photometric (FPD) detection.

A 5-g sample of soil spiked with 4 μg/g diethyl malonate and 1 μg/g tributyl phosphate was warmed slightly for 5 min. A minitube was then held approximately 2–5 mm above the soil and the headspace air (100 ml) was drawn through the minitube using a syringe. *n*-Alkane probes were then added to the minitube using the vapourizing unit and analyzed by TD–GC with simultaneous FID–FPD monitoring. The spiked soil was also extracted with acetone (5 ml) for 15 min in an ultrasonic bath and an aliquot of this solution (1 μl) was loaded onto a minitube to verify the presence of these compounds.

Instrumental

GC analyses were performed with a HP 5890 (Hewlett-Packard, Avondale, PA, U.S.A.) gas chromatograph equipped for simultaneous FID and FPD detection. Four different megabore (15 m × 0.53 mm I.D.) fused-silica columns, DB-1, DB-5, DB-1701 and DBWAX (J&W Scientific, Rancho Cordova, CA, U.S.A.), were used for GC retention index monitoring. Each column was held at 50°C for 2 min followed by a ramp of 10°C/min to the upper temperature limit of the column. Minitubes loaded with analytes were desorbed on an automated thermal desorption unit (ATDU) at 240°C for 5 min. High-purity helium (Liquid Carbonic, Scarborough, Canada) was used as the carrier gas at a flow-rate of 6 ml/min. Five chromatographic analyses were carried out for each analyte on each column to determine GC retention index reproducibility. Data acquisition and handling were performed with a Nelson Analytical Model 6000 data system.

RESULTS AND DISCUSSION

Method validation

Minitubes were loaded using the vapourizing unit, as this method of loading followed by TD–GC analysis has been shown to produce chromatographic performance equivalent to traditional syringe injection techniques [19]. The *n*-alkane probes were then loaded onto the same minitube and the minitube analyzed by TD–GC. In order to validate the subsequent loading of minitubes with the *n*-alkanes, it was necessary to demonstrate that: (i) the secondary loading of the probes did not degrade chromatographic performance and (ii) that loading using the GC injector produced the same retention indices as actual vapour sampling. Fig. 1 illustrates the TD–GC analysis of a minitube that had been initially loaded with soman, triethyl phosphate, mustard, and methyl salicylate and subsequently loaded with the $C_{10}-C_{12}$ *n*-alkane probes. It was evident from the chromatogram that subsequent loading of the probes did not affect the chromatographic resolution of the system. Peak shape and resolution were equivalent to syringe injection and previously published TD–GC data [19].

To demonstrate that retention indices obtained with the vapourizing loader were equivalent to those obtained by air sampling, a series of experiments were conducted with five simulants vapourized in a sealed chamber and the vapour collected under vapour sampling conditions. Table I lists the GC retention indices by both methods
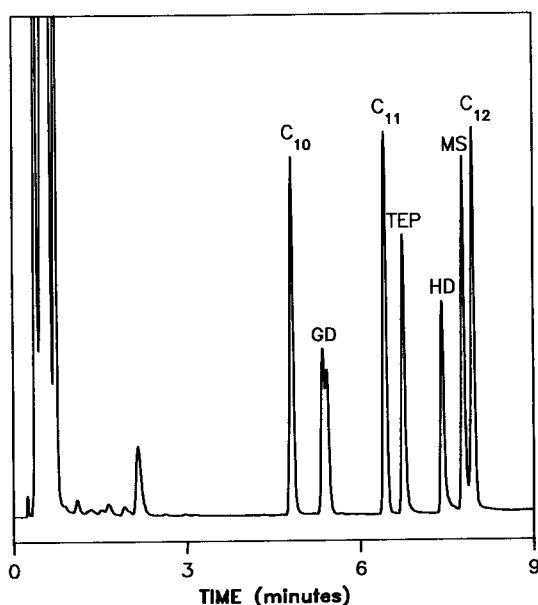

Fig. 1. TD–GC–FID chromatogram of soman (GD), triethyl phosphate (TEP), mustard (HD), methyl salicylate (MS) and $C_{10}-C_{12}$ *n*-alkanes. Probes were added to minitube subsequent to initial loading analytes. Column conditions: 15 m × 0.53 mm I.D. DB-5, helium flow-rate of 6 ml/min, temperature program of 50°C (2 min), 10°C/min to 120°C. Desorption conditions: desorption temperature, 240°C and cycle time, 5 min.

TABLE I

COMPARISON OF RETENTION INDICES FROM VAPOUR SAMPLING AND DIRECT LOADING

Compound	Retention index (mean $\pm$ S.D., $n = 5$)	
	Direct loading	Vapour chamber
Dimethyl sulphoxide	820.1 $\pm$ 0.4	820.5 $\pm$ 0.6
Diethyl malonate	1069.2 $\pm$ 0.1	1069.2 $\pm$ 0.1
Triethyl phosphate	1120.5 $\pm$ 0.2	1121.3 $\pm$ 0.2
Methyl salicylate	1188.8 $\pm$ 0.1	1188.6 $\pm$ 0.2
Tributyl phosphate	1647.4 $\pm$ 0.1	1647.9 $\pm$ 0.2

and clearly illustrates that the retention indices were independent of the loading method.

Compound database

Table II lists the GC retention indices calculated for fourteen compounds on four fused silica capillary columns of varying polarity using the HP 5890 GC. Sesquimustard [(2-chloroethylthio)ethyl 2-chloroethyl sulphide] and bis[(2-chloroethylthio)ethyl] ether were not included for the DBWAX column as they were not eluted by the upper temperature limit of that column. Error estimates for the indices were based on the standard deviation from five replicate analyses. The results obtained

TABLE II

GC RETENTION INDICES OF CHEMICAL DEFENCE RELATED COMPOUNDS

Compound	Retention index (mean $\pm$ S.D., $n = 5$)			
	DB-1	DB-5	DB-1701	DBWAX
Nerve agents				
Sarin	789.1 $\pm$ 0.1	817.0 $\pm$ 0.4	954.5 $\pm$ 0.3	1296.6 $\pm$ 0.1
Soman	1011.6 $\pm$ 0.1	1038.0 $\pm$ 0.1	1178.7 $\pm$ 0.1	1478.4 $\pm$ 0.3
	1016.0 $\pm$ 0.1	1042.4 $\pm$ 0.1	1184.6 $\pm$ 0.1	1489.6 $\pm$ 0.3
Vesicants (and related impurities)				
1,4-Thioxane	856.8 $\pm$ 0.3	884.5 $\pm$ 0.1	966.8 $\pm$ 0.1	1333.8 $\pm$ 0.1
1,4-Dithiane	1027.5 $\pm$ 0.2	1067.7 $\pm$ 0.1	1163.5 $\pm$ 0.1	1611.6 $\pm$ 0.1
Mustard	1136.2 $\pm$ 0.1	1175.5 $\pm$ 0.1	1327.9 $\pm$ 0.3	1846.2 $\pm$ 0.4
Bis (2-chloroethyl) disulphide	1344.9 $\pm$ 0.2	1402.7 $\pm$ 0.1	1566.0 $\pm$ 0.1	2165.9 $\pm$ 0.1
2-Chloroethyl (2-chloroethoxy) ethyl sulphide	1426.0 $\pm$ 0.9	1476.0 $\pm$ 0.1	1659.4 $\pm$ 0.1	2274.2 $\pm$ 0.1
Sesquimustard	1632.0 $\pm$ 1	1694.0 $\pm$ 0.1	1923.1 $\pm$ 0.1	
Bis[(2-chloroethylthio)ethyl]ether	1921.0 $\pm$ 2	1987.8 $\pm$ 0.2	2240.7 $\pm$ 0.2	
Simulants				
Dimethyl sulphoxide	781.9 $\pm$ 0.3	829.2 $\pm$ 0.5	1043.1 $\pm$ 0.1	1506.7 $\pm$ 0.5
Diethyl malonate	1038.2 $\pm$ 0.1	1068.8 $\pm$ 0.1	1195.9 $\pm$ 0.1	1500.5 $\pm$ 0.4
Triethyl phosphate	1088.3 $\pm$ 0.1	1121.5 $\pm$ 0.2	1287.8 $\pm$ 0.1	1688.6 $\pm$ 0.8
Methyl salicylate	1175.5 $\pm$ 0.1	1203.2 $\pm$ 0.1	1306.6 $\pm$ 0.3	1801.8 $\pm$ 0.8
Tributyl phosphate	1615.6 $\pm$ 0.1	1638.7 $\pm$ 0.1	1817.7 $\pm$ 0.1	2157.7 $\pm$ 0.3

for the fourteen compounds were similar to those previously reported by D'Agostino and Provost [13] using on-column injection. Slight GC retention index differences were likely due to the differences in column diameter (0.32 mm *vs.* 0.53 mm) of variations in the thickness of the stationary phase (0.25 μm *vs.* 1.0 μm).

Simultaneous FID–FPD detection

Two detectors (FID and FPD) were operated in parallel by splitting the column effluent with a glass splitter and two short lengths (30 cm) of deactivated fused-silica column. The sections of deactivated column were then trimmed to bring the retention times of a reference peak (triethyl phosphate) to within 0.006 min of each other on the two detectors. The two detectors, operating in parallel, provided more specific and sensitive analysis of phosphorus and sulphur containing compounds with the added benefit of being able to determine retention indices using *n*-alkane probes. Fig. 2 illustrates the universal nature of the flame ionization detection and the specific response of the flame photometric detector in phosphorus and sulfur modes for a mixture of CW agents and simulants. All the compounds were detected by FID; only sarin, soman, triethyl phosphate and tributyl phosphate were detected by FPD in phosphorus mode and only the mustard peak was detected in sulfur mode. A small response (cross-talk) for mustard was observed on the phosphorus channel.

Water and soil samples

A sample of tap water (2 ml), spiked with triethyl phosphate (20 μg/g), was purged for 30 min with nitrogen and the volatiles trapped on a Tenax minitube. Fig.
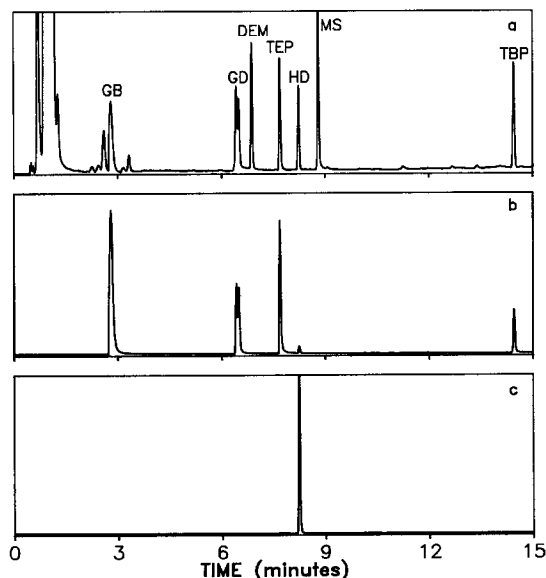

Fig. 2. TD–GC chromatograms of simultaneous detection by (a) FID, (b) FPD (phosphorus mode) and subsequent (c) FPD (sulfur mode) analysis of sarin (GB), soman (GD), diethyl malonate (DEM), triethyl phosphate (TEP), mustard (HD), methyl salicylate (MS) and tributyl phosphate (TBP). Column conditions: 15 m × 0.53 mm I.D. DB-5, helium flow-rate of 6 ml/min, temperature program of 50°C (2 min), 10°C/min to 180°C. Desorption conditions: desorption temperature, 240°C and cycle time, 5 min.

3 illustrates simultaneous thermal desorption flame photometric and flame ionization chromatograms. FPD (phosphorus mode) was used to detect triethyl phosphate at approximately the 250 pg level, while FID, operated in parallel, was used to determine the GC retention times of the *n*-alkane probes. A retention index of 1091.3 was calculated for triethyl phosphate, which was in good agreement with the previously determined value of 1088.3 (Table II). No peaks were detected in the chromatograms of the blanks run for this and subsequent samples.   ·

The headspace above a soil sample (5 g), spiked with diethyl malonate (4 μg/g) and tributyl phosphate (1 μg/g), was sampled with a minitube and analyzed by TD–GC with simultaneous FID–FPD detection (Fig. 4). GC retention indices of 1038.4 and 1613.6 were determined for diethyl malonate and tributyl phosphate respectively. Diethyl malonate was easily detected, at approximately the 25 ng level, by FID and tributyl phosphate, while not detected by FID, was clearly visible, at approximately the 20 pg level with the FPD. Previous experience illustrated the limitations of headspace analysis for samples containing relatively non-volatile components. The soil was therefore also extracted with 5 ml of acetone and 1 μl of this extract was loaded onto a minitube for TD–GC analysis. Simultaneous FID–FPD chromatograms of the acetone extract of the soil are illustrated in Fig. 5. The peak for diethyl malonate was difficult to discern from the background chemical noise and tributyl phosphate could not be detected during FID analysis, while the FPD (phosphorus mode) chromatogram confirmed the presence of tributyl phosphate.
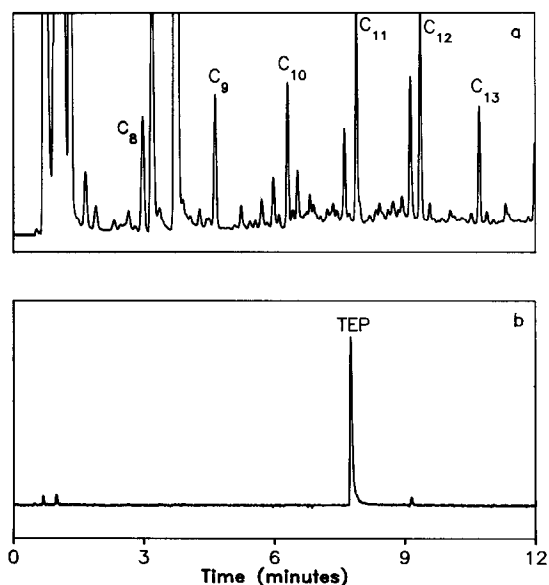

Fig. 3. TD–GC chromatograms of simultaneous detection by (a) FID and (b) FPD (phosphorus mode) of a water sample spiked with 20 μg/g triethyl phosphate (TEP) and subsequently loaded with *n*-alkane probes. Column conditions: 15 m × 0.53 mm I.D. DB-1, helium flow-rate of 6 ml/min, temperature program of 50°C (2 min), 10°C/min to 150°C. Desorption conditions: desorption temperature, 240°C and cycle time, 5 min.
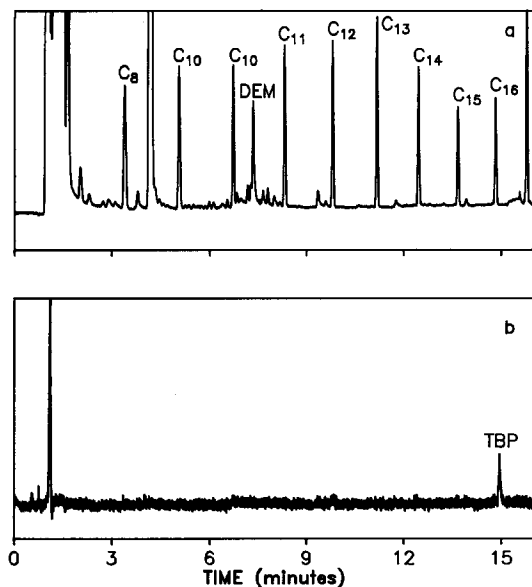
Fig. 4. TD–GC chromatograms of simultaneous detection by (a) FID and (b) FPD (phosphorus mode) of headspace above soil sample spiked with 4 μg/g diethyl malonate (DEM) and 1μg/g tributyl phosphate (TBP). Column conditions: 15 m × 0.53 mm I.D. DB-1, helium flow-rate of 6 ml/min, temperature program of 50°C (2 min), 10°C/min to 190°C. Desorption conditions: desorption temperature, 240°C and cycle time, 5 min.
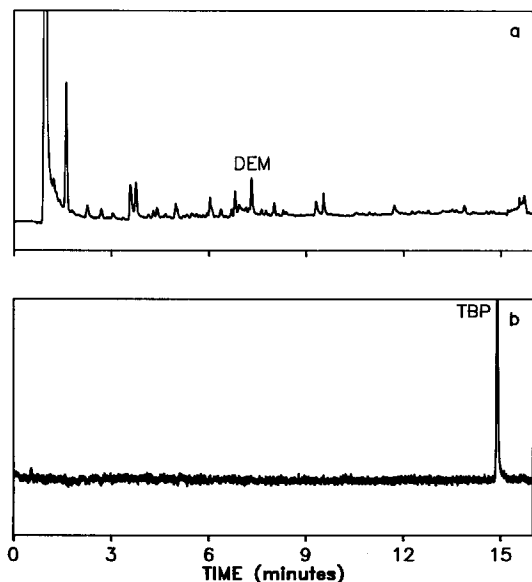

Fig. 5. TD–GC chromatograms of simultaneous detection by (a) FID and (b) FPD (phosphorus) mode of acetone extract of a soil sample spiked with 4 μg/g diethyl malonate (DEM) and 1 μg/g tributyl phosphate (TBP). Column conditions: 15 m × 0.53 mm I.D. DB-1, helium flow-rate of 6 ml/min, temperature program of 50°C (2 min), 10°C/min to 190°C. Desorption conditions: desorption temperature, 240°C and cycle time, 5 min.

CONCLUSIONS

Retention index monitoring using thermal desorption gas chromatographic analysis has been shown to be useful in the identification of compounds of chemical defence interest in environmental matrices. A database of GC retention indices for chemical warfare agents and simulants was compiled and, in conjunction with simultaneous flame ionization and flame photometric detection, applied to the identification of triethyl phosphate, tributyl phosphate and diethyl malonate in water and soil samples.

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