CHROMSYMP. 1085

GAS CHROMATOGRAPHIC PROPERTIES OF THE M SERIES OF UNIVERSAL RETENTION INDEX STANDARDS AND THEIR APPLICATION TO PESTICIDE ANALYSIS

A. MANNINEN*, M.-L. KUITUNEN and L. JULIN

Nordion Instruments Oy Ltd., P.O. Box 1, SF-00371 Helsinki (Finland)

SUMMARY

The suitability of alkylbis(trifluoromethyl)phosphine sulphides for use as universal retention-index standards has been confirmed. In routine work, the M series were detected at the level of 0.4–0.6 pmol with flame ionization detection (FID), 2–7 fmol with alkaline thermionization detection (ATD) and 3–5 fmol with electron-capture detection (ECD). The sensitivities of ATD and ECD are so much greater than that of FID that their simultaneous use with FID is not possible. The sensitivities of ECD and ATD are similar enough that parallel use is possible. Examples of two-channel retention-index monitoring of pesticides from real samples are given.

INTRODUCTION

Measurement of the same retention indices for solutes by use of different element-specific detectors is impossible in the absence of a universal standard series detectable with all common detectors. This problem has been solved in part by the development of element-specific index series. Straight chain dialkyl sulphides have been proposed for the detection of sulphur-containing compounds, using flame photometric detection (FDP)[1] and a series of trialkylamines has recently been developed for the detection of compounds containing nitrogen and phosphorus, *e.g.*, for pesticide analysis (Fig. 1)[2].

The Finnish Research Project on the Verification of Chemical Disarmament has been studying sensitive and reliable methods for the monitoring of chemical agents from environmental samples[3]. One part of the work has been to find universal multidetector index standards for gas chromatographic (GC) analysis. The first useful standards (P series) were developed in 1979 (Fig. 1). These give a response to flame ionization (FID), alkaline thermionization (ATD) and flame photometric detection. The disadvantages of the series were the poor volatility when compared with the alkanes and the absence of a response to electron capture detection (ECD). Despite its versatility, this series has not found general acceptance, perhaps because it was not easily available.

The next step was the synthesis of a real multidetector standard series, alkyl bis(trifluoromethyl)phosphinothioates. These compounds are volatile and give a re-

$$S[(CH_2)_nCH_3]_2 \qquad N[(CH_2)_nCH_3]_3$$
$$\qquad I \qquad\qquad\qquad\qquad II$$

$$\begin{array}{cc} S & S \\ \| & \| \\ CH_3-P-O(CH_2)_nCH_3 & CF_3-P-O-(CH_2)_nCH_3 \\ | & | \\ CH_3 & CF_3 \\ III & IV \end{array}$$
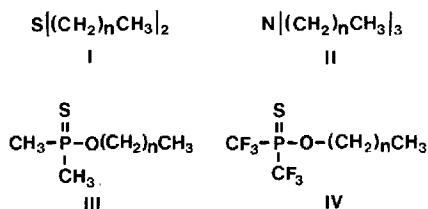
Fig. 1. Some retention index standard series proposed for element-specific detectors. I = Dialkyl sulphides; II = trialkylamines; III = alkyl dimethylphosphinothioates (P series) and IV = alkyl bis(trifluoromethyl)phosphinothioates; n = 0, 1, 2, etc.

sponse with all common GC detectors. However, they are not stable enough, undergoing thiono–thiolo rearrangement at high temperatures when chromatographed on polar columns.

The most recent step has been the synthesis of the thermally stable multidetector index series of alkylbis(trifluoromethyl)phosphine sulphides (M series), which has the specific label atoms at one end of an hydrocarbon chain (Fig. 2). The M series is currently being applied to routine retention index monitoring of environmental pollutants and pesticide residues in foods. These sulphides are stable in the usual GC solvents such as hexane, ethyl acetate, dichloromethane and methanol. In strongly basic solutions they are hydrolysed and fluoroform is formed.

The goal of the present study was to obtain more information about these standards, the sensitivity of various detectors to them, the response linearity of individual components and their detection limits. The suitability of the M series for two-channel retention-index monitoring was also considered.

EXPERIMENTAL

The response measurements were carried out on a MICROMAT HRGC 412 gas chromatograph equipped with parallel Nordion OV-1701 and Nordion SE-30 fused-silica columns having a film thickness of 0.25 μm and dimensions of 25 m × 0.32 mm I.D. The columns were connected to flame ionization, alkaline thermionization and electron-capture detectors for each set of experiments. The temperature programme was from 60 to 270°C at 10°C/min, the injector temperature was 250°C and the detector temperature 280°C. The helium gas velocity was 1.3 ml/min for both columns. The alkaline thermionization detector was adjusted so that 7.5 pg of mal-

$$\begin{array}{c} FPD \\ ATD \quad \downarrow \quad PID \\ \searrow \quad S \quad \nearrow \\ \quad\quad \| \\ CF_3-P-(CH_2)_nCH_3 \\ \quad | \\ \nearrow \quad CF_3 \quad \downarrow \\ ECD \quad\quad\quad FID \end{array}$$
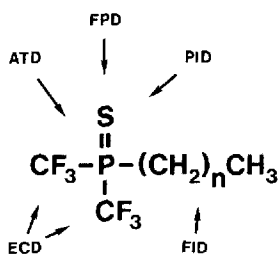
Fig. 2. The universal retention index standard series, alkylbis(trifluoromethyl)phosphine sulphides, for use with GC detectors.

athione and 36 pg of azobenzene could be detected (hydrogen flow-rate 3 ml/min). With the electron-capture detector the detection limit for lindane was set at 2 pg (argon–methane flow-rate 20 ml/min). The samples were injected with a splitless time of 45 s.

Alkylbis(trifluoromethyl)phosphine sulphides were prepared by Nordion Instruments Oy Ltd. Components M_8 to M_{20} with even carbon numbers were diluted in hexane (Mallinckrodt, Nanograde) to give concentrations in the basic mixture of $2.65 \cdot 10^{-4}$ M. The concentration of M_{20} was $2.32 \cdot 10^{-4}$ M. The average peak areas were calculated from five injections.

The sweet pepper extract was kindly supplied by the Finnish Customs Laboratory. The sample was chromatographed on parallel Nordion SE-54 and Nordion OV-1701 columns, both connected to an electron-capture detector. Temperature programme: 2 min at 50°C, then to 150°C at 20°C/min and to 270°C at 6°C/min. The injector temperature was 250°C and the detector temperature was 300°C. Splitless time: 45 s.

The analytical data for the pesticides were stored in the library of the versatile MICMAN software, which allows monitoring of all library compounds. The pesticides were identified using the cubic spline retention-index method. Also available for identification purposes are the absolute retention time, relative retention time, linear retention index and Kováts index. Nine different methods are available for quantitative analyses.

RESULTS AND DISCUSSION

The components of the M series are comparatively non-polar, and on the non-polar phase SE-54 they differ little in elution behaviour from those of the alkane standards[3]. The linear correlation between the retention indices of nine different chemical agents based on alkanes and M standards is shown in Fig. 3 (earlier results).

Due to the discrimination of high-molecular-weight components by the split-type injector[4] and to the sensitivity of FID to the number of carbon atoms of the standards, the relative responses ECD/FID and ATD/FID decrease as the molecular weight increases (Table I). However, the ratio ECD/ATD is constant at about 2.25
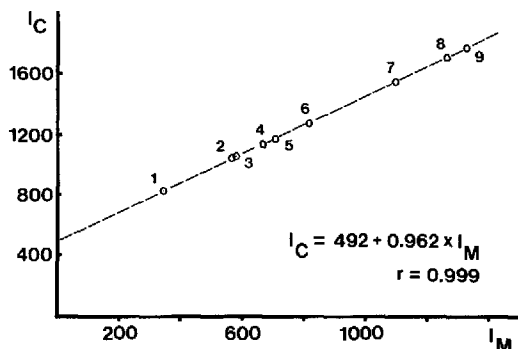

Fig. 3. Linear dependence between alkane-based retention indices I_C, and M series-based indices, I_M, for nine chemical agents (plotted from data of ref. 3, p. 215). Conditions: SE-54, 15 m × 0.32 mm I.D., 0.25 µm; 40 to 300°C at 5°C/min.

TABLE I

RELATIVE RESPONSES OF M STANDARDS TO VARIOUS DETECTORS

Standard	ECD/FID	ATD/FID	ECD/ATD
M_8	630	268	2.35
M_{10}	504	221	2.28
M_{12}	410	189	2.17
M_{14}	345	161	2.14
M_{16}	311	141	2.21
M_{18}	300	128	2.34
M_{20}	289	128	2.26

because the amount of the label atoms for these detectors is constant for every component of the series. The sensitivity of ECD is about 300–600 and that of ATD is about 100–300 times as great as the sensitivity of FID, depending on the component.

The response linearity was good for ECD and ATD (Figs. 4 and 5), but there was some deviation from linearity with FID. The standards were not decomposed or absorbed by either column.

The electron-capture detector was not adjusted to its maximum sensitivity, but a practical working level was used. The gas flow-rates for ATD were adjusted so that the nitrogen–phosphorus mode was obtained. The detection limits in Table II were calculated from peak heights twice as large as the noise. The similarity of the detection limits for the components of the M series allows ATD and ECD to be combined for two-channel retention-index monitoring. Simultaneous use of FID with these detection modes is not possible because of its much poorer sensitivity.

The most important advantage of the M series is that the same indices are obtained with all the usual GC detectors. Conversions such as those in Fig. 3 are not necessary and one source of error is avoided. The chemical and physical properties of the M series will often differ from those of the solutes, resulting perhaps in poorer
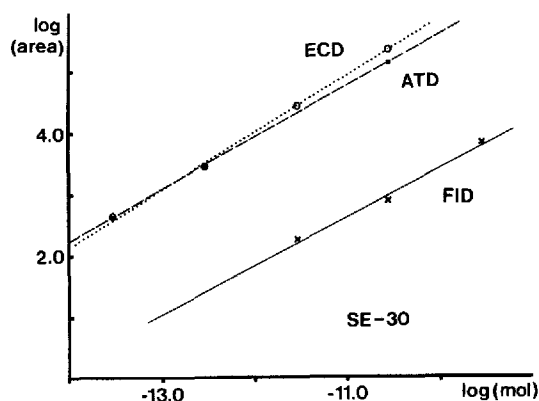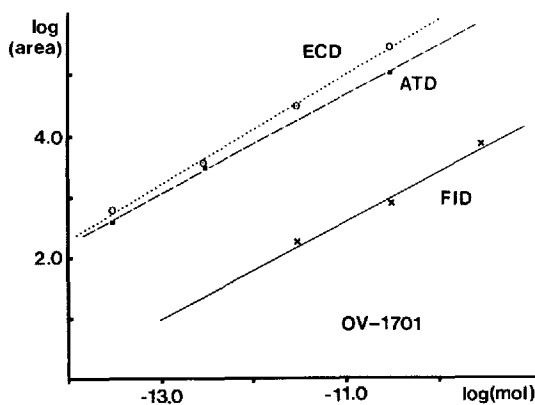

Fig. 4. Linearity of responses of the component M_{14} to ECD, ATD and FID on a SE-30 column.

Fig. 5. Linearity of responses of the component M_{14} to ECD, ATD and FID on an OV-1701 column.

TABLE II

DETECTION LIMITS FOR THREE COMPONENTS OF THE M SERIES

Component		FID	ATD	ECD
M_8	(fmol)	400	2	3
	(pg)	140	0.7	0.8
M_{14}	(fmol)	300	3	3
	(pg)	130	1.0	1.2
M_{20}	(fmol)	600	7	5
	(pg)	280	3.4	2.5

reproducibility of retention indices when the chromatographic conditions change slightly. This disadvantage is inherent in all general purpose index standard series. The best reproducibility is obtained when sample components chemically similar to the solutes are used as index standards[5]. However, in many monitoring tasks, the concentrations of the background compounds and of the compounds to be detected vary too widely for them to be used as index standards. For instance, the background of a real sweet pepper extract is very clean in ECD analysis (Fig. 6). It is better to
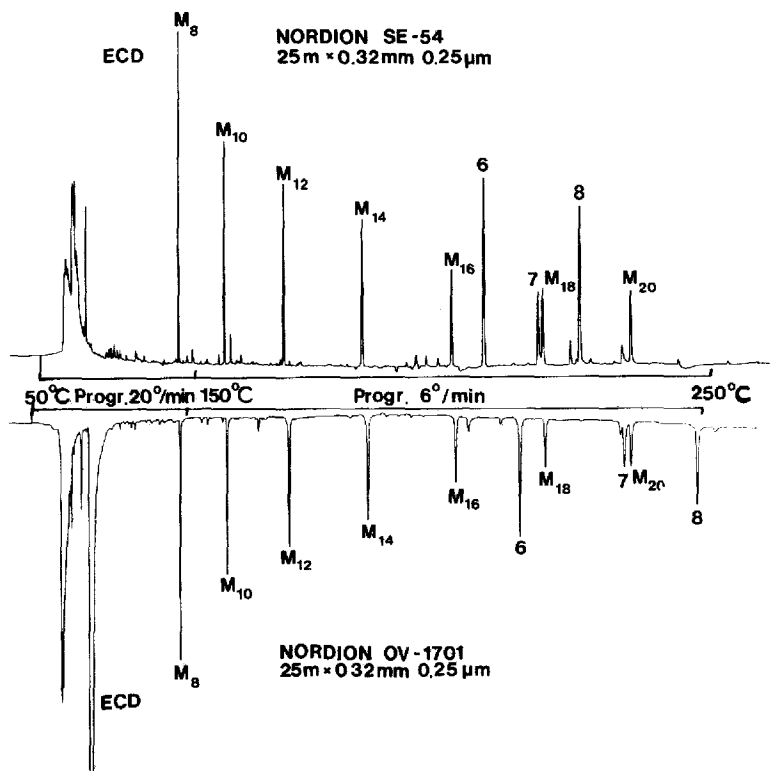

Fig. 6. Two-channel analysis of a sweet pepper sample on SE-54 and OV-1701 columns with two electron-capture detectors. Pesticides: 6 = Endosulfan alfa; 7 = Endosulfan beta and 8 = Endosulfan sulphate.

TABLE III

A SWEET PEPPER ANALYSIS REPORT (FIG. 6)

t_R = Measured retention time; IDNO = the number of a reference compound, when relative retention times are used; ID-PARA = the calculated identification parameter, here the retention index; DIFF = the difference between measured and library identification parameters; REFSTD = the reference standard used for the quantitation, where S = the standard compound, A = the compound to be analysed. The cubic spline retention-index method of identification was used.

| Library No.	Name	$t_R(s)$	Peak Area	IDNO	ID-PARA	DIFF	REFSTD	Amount (ppm)
1	M_{16}	798.76	18 742	0	1600.000	0.000	S:0	0.10000
		823.24	15 201	0	1600.000	0.000	S:0	0.10000
2	M_{20}	1147.04	15 968	0	2000.000	0.000	S:0	0.10000
		1164.04	11 468	0	2000.000	0.000	S:0	0.10000
6	Endosulfan alfa	861.44	38 330	0	1670.517	0.417	A:1	0.15809
		947.60	29 570	0	1743.117	−0.883	A:1	0.16301
7	Endosulfan beta	966.28	18 663	0	1789.229	0.279	A:2	0.10766
		1151.04	13 173	0	1984.363	−0.887	A:2	0.09863
8	Endosulfan sulphate	1047.60	34 779	0	1883.292	0.542	A:2	0.21024
		1292.80	21 655	0	2154.886	−0.964	A:2	0.19459
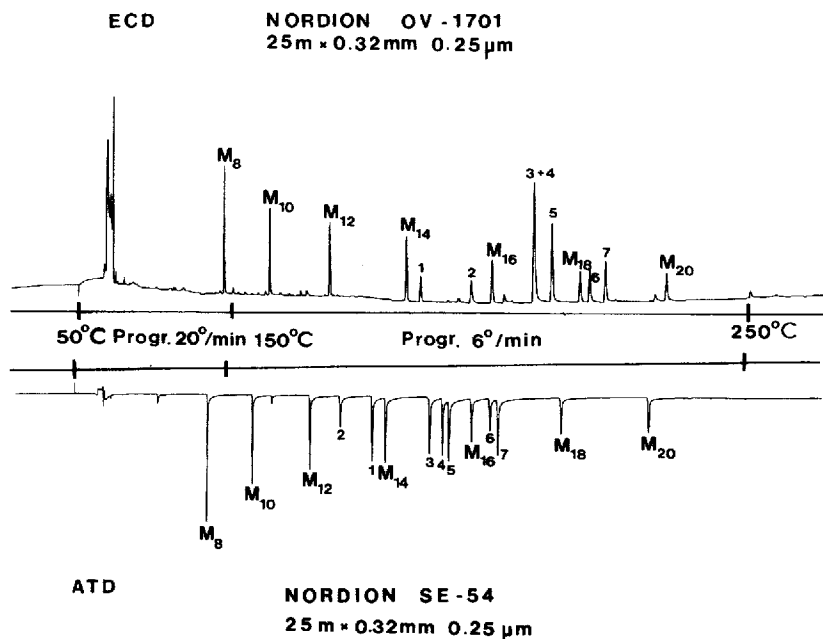
Fig. 7. Two-channel analysis of a pesticide mixture on SE-54 and OV-1701 columns with ATD and ECD. Pesticides: 1 = Diazinon; 2 = Dimethoate; 3 = Fenitrothion; 4 = Malathion; 5 = Parathion; 6 = Mecarbam and 7 = Methidathion.

increase the reliability of the identification by using two columns of different polarities. In the case of the pepper analysis, the retention indices of Endosulfan isomers differed by 100–300 index units when determined on SE-54 and OV-1701 (Table III). When the compounds to be analysed have a response to several element-specific detectors, the reliability of the identification can be increased further by using columns of different polarities and different element-specific detectors (Fig. 7).

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