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IMPROVED PRECISION GAS CHROMATOGRAPHIC METHOD FOR RETENTION INDEX MONITORING WITH A CALIBRATION DETECTOR

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SUMMARY

An improvement in the multidetector retention index monitoring method is presented. The method is based on the use of a sensitive and selective calibration detector (e.g., alkali thermionic detector or electron-capture detector) for detecting suitable labelled members of the alkane series in the split effluent from a fused-silica capillary column. The retention times of the homologous series are then used for calculating the retention indices of the sample components detected with an analytical detector that measures a different property of the other part of the splitter effluent. In this method, the sample contains an internal scale which does not affect sample composition, but gives a clear and accurate reference for peak identification.

INTRODUCTION

Improved quality of capillary columns, including a better knowledge of the chemical structure of stationary phases, considerably increases the significance of retention parameters as an aid to peak identification in target compound monitoring. Column-to-column reproducibility, as determined in retention index units, is now typically better than ± 0.5 unit for many stationary phases. Especially when selective detectors can be used, retention-index monitoring (RIM) is a cost-effective alternative to some gas chromatographic-mass spectrometric (GC-MS) applications in target compound analysis.

In earlier work^{1,2} we have described a promising method based on two-channel RIM with two similar or different capillary columns and two similar or different detectors. In view of the obvious advantages of having retention index standards structurally close to the compounds to be analysed, a phosphorus-containing homologous series was synthesized to be used for chemical warfare agent and pesticide target compound analysis³. With *n*-alkanes as retention index standards, phosphorus-specific alkali thermionic detection (ATD) could not be used and the polarities of standards and target compounds were too different for long-term reproducibility of retention indices in practical environmental and food analysis.

With our new multidetector retention index (MDRI) standards we can now make use of the two-channel-precision GC method, based on two different capillary columns with a two-ATD or two-electron-capture detection (ECD) system. With a pattern recognition algorithm⁴ the assignment of retention index standard peaks can be automated and, using the retention times of these peaks, the retention indices of unknown peaks are automatically calculated. Thereafter, the indices are compared with corresponding reference data in a disk memory file and the compounds on the two columns with sufficiently small deviations are selected and reported, along with their respective concentrations (Fig. 1).

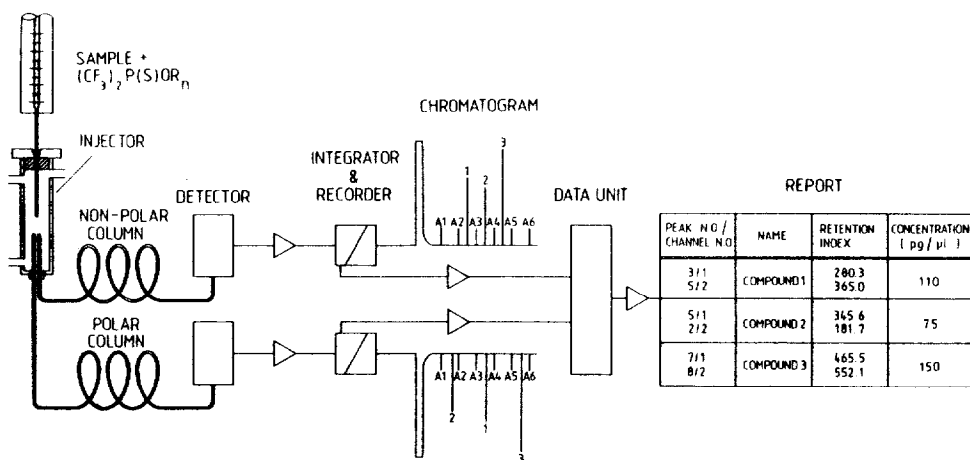


Fig. 1. Scheme of the basic two-channel retention index monitoring system.

The purpose of this paper is to demonstrate a new calibration method that further improves the usefulness of the RIM method and permits a preliminary characterization of unknown samples by their retention behaviour.

With very complex samples, it is not always desirable to add internal retention index standards to the sample. The standards added may sometimes complicate the quantitative determination of target compounds, and some samples may also contain complex peak patterns in a narrow area (*e.g.*, toxaphene) where internal calibration peaks are not always desirable. It is also difficult to assign peaks of homologues manually in complex samples.

These problems can be solved if the column is equipped with a 1:1 outlet splitter and if the splitter capillaries are connected to an analytical detector and to a suitable calibration detector. If flame-ionization detection (FID) is used for analytical detection, the most useful calibration detector is one that is at least two orders of magnitude more sensitive and specific for certain characteristics that do not appear in the analytical samples. ATD is a very good example, particularly with a phosphorus-labelled homologous series as an internal retention index standard. Fig. 2. shows the principle of using a specific calibration detector for retention-index determinations. A well known related example in GC-MS monitoring is the use of deuterium-labelled standards for selected-ion monitoring analysis. There the selectivity is obtained by the 1 *m/z* increase for each deuterium atom in a molecule.

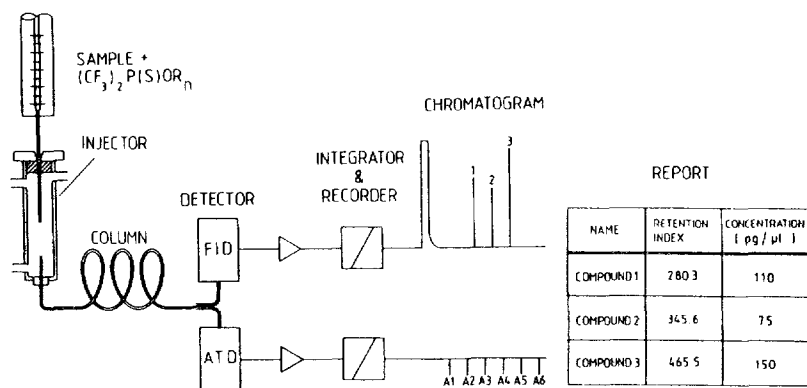


Fig. 2. Scheme of the new RIM method with the retention index standard-specific calibration detector.

EXPERIMENTAL

An Orion-Micomat microcomputer-controlled precision gas chromatograph, especially developed for routine capillary GC, and an immobilized SE-54 (0.25- μm film thickness) fused-silica capillary column from Orion Analytica were used. Fig. 3 shows the structure of the low-dead-volume deactivated fused-silica effluent splitter used. With this construction, it was not necessary to use make-up gas for the split-purging. The GC conditions are shown in each figure.

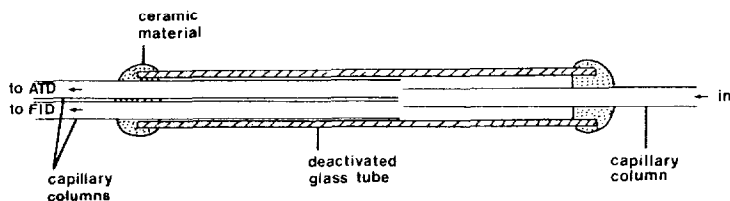


Fig. 3. Splitter (1:1), constructed from a deactivated glass tube and fused-silica columns. Deactivation by silylation, according to Grob⁵.

The splitter was constructed from a 100 x 0.9 mm I.D. glass tube, into which two capillary columns could just be inserted. A modified four-way splitter with make-up gas was also constructed, but for the present applications, the simple three-way construction was satisfactory and more useful. The retention index standards used were bis(trifluoromethyl)thiophosphate-labelled *n*-alkanes³.

RESULTS AND DISCUSSION

Small amounts (10–100 pg, on-column) of each phosphorus-labelled homologue is added to the samples to be analysed. With appropriate attenuation of the analytical (FID) and calibration (ATD) detectors, no interference from the calibration peaks is observed in the analytical channel.

Absolute retention times cannot be used for identification, when the chromato-

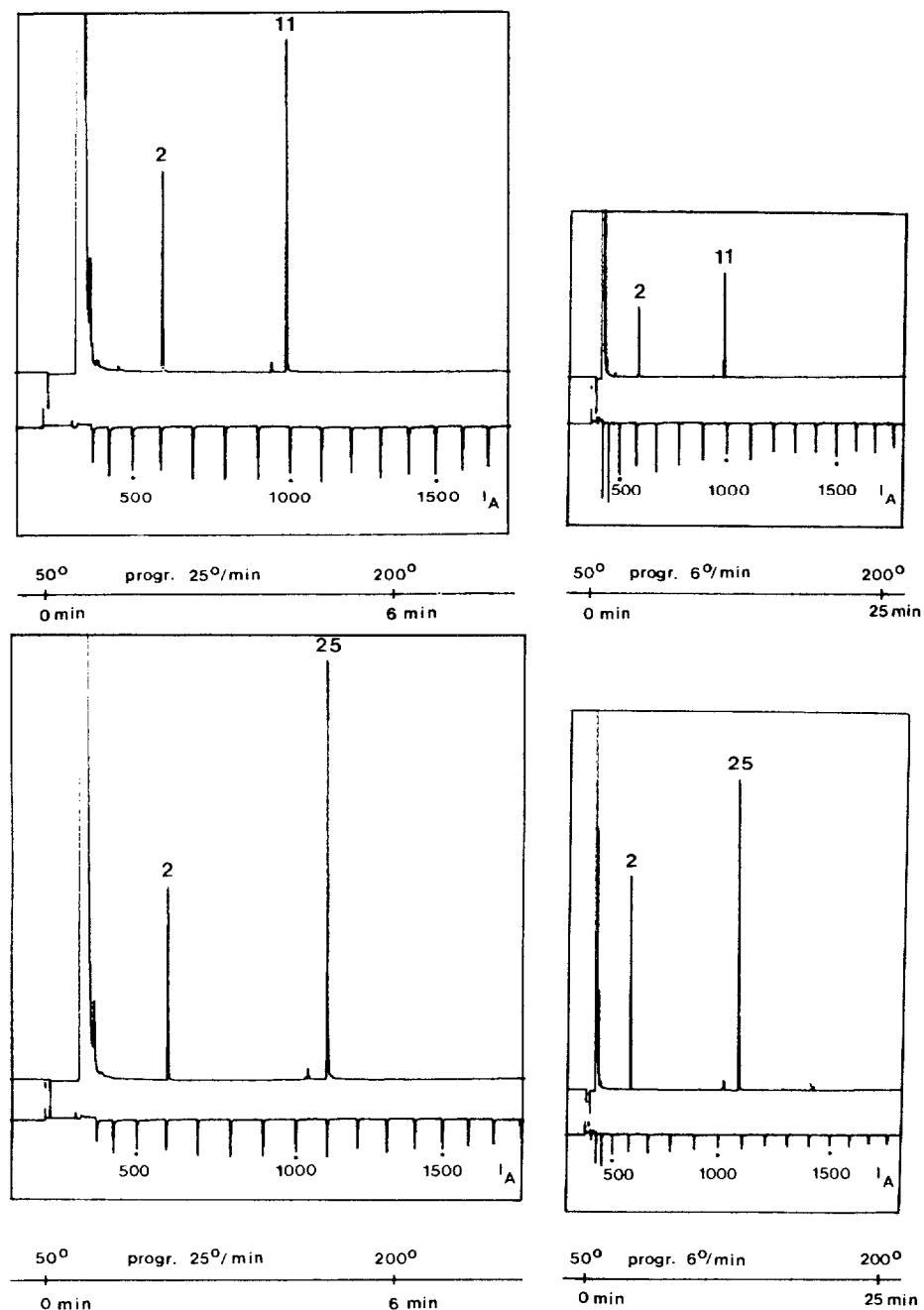


Fig. 4. Gas chromatograms of three model compounds at a slow and a rapid programming rate. Column: bonded SE-54, 10 m \times 0.32 mm I.D. (0.25 μ m). Injector, 240°C; Detectors, 260°C; splitting ratio, 1:20; carrier gas, helium. Upper trace, FID (analytical channel, attenuation 128); lower trace, ATD (calibration channel, attenuation 1024).

TABLE I

RETENTION INDICES OF THREE MODEL COMPOUNDS, DETERMINED BY USING A-INDEX STANDARDS [*n*-ALKYL BIS(TRIFLUOROMETHYL) THIOPHOSPHINATES], BONDED SE-54 AS STATIONARY PHASE AND THREE DIFFERENT PROGRAMMING RATES.

The temperature programme was started from 50°C.

Compound	I_A		
	6°C/min	10°C/min	25°C/min
2-Pentyl butanoate (2)	585.0	587.3	589.8
Hexyl hexanoate (11)	968.3	696.8	974.5
β -Ionone (25)	1069.3	1074.2	1086.0

graphic conditions (temperature programme, carrier gas velocity) or injection mode differ from one analysis to another. With retention indices, a preliminary check is possible, even when the temperature programmes differ, because the temperature dependence of the retention indices is usually not very marked. On the other hand, if the retention indices of some compounds undergo a very significant change with temperature, this can be used as a diagnostic tool for identification (a new parameter, in ad-

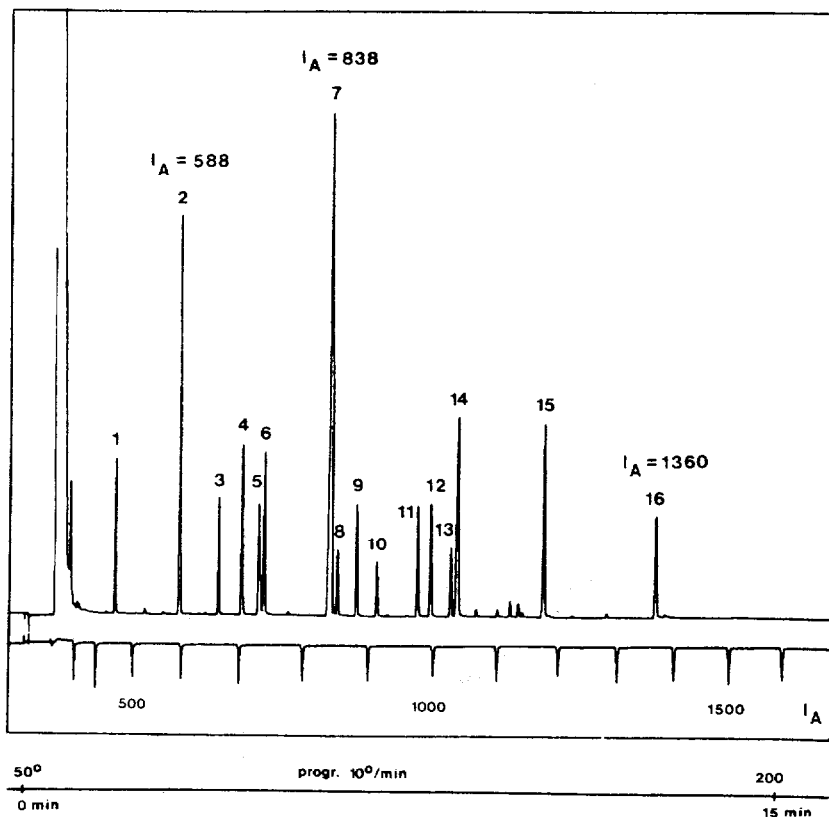


Fig. 5. Separation of some model compounds. Column and chromatographic conditions (except the programming rate) as in Fig. 4.

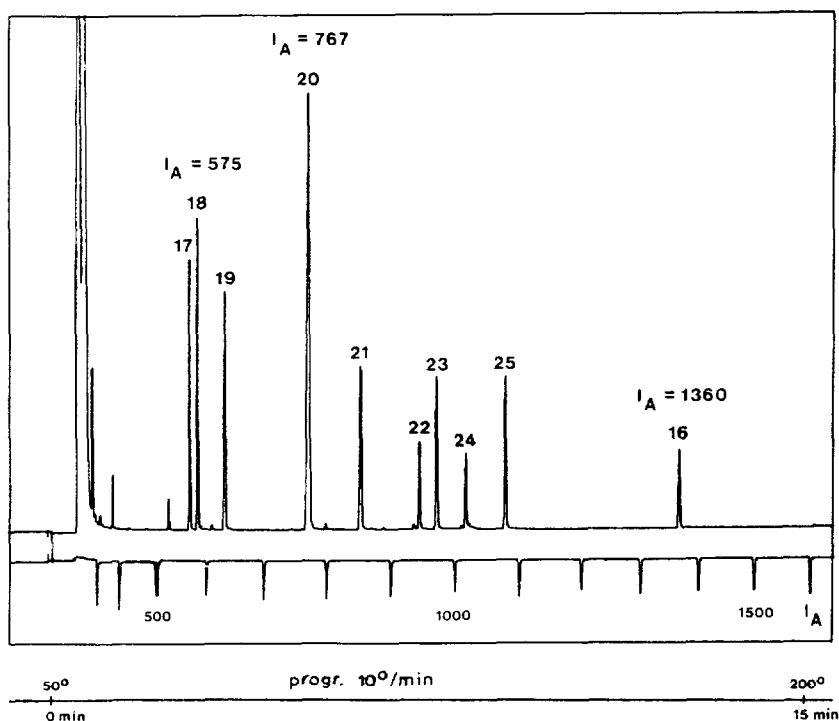


Fig. 6. Separation of some typical aroma compounds in berries. Column and chromatographic conditions as in Fig. 5.

dition to the retention indices determined on different stationary phases and the detector response ratios, measured with different, possibly selective, detectors). Polycyclic aromatic hydrocarbons are examples of this kind of compound.

When the temperature of the column is rapidly raised, say at $25^{\circ}\text{C}/\text{min}$, and the column is short, e.g., 5 m, it is possible to obtain an approximate idea on the com-

TABLE II
LIST OF COMPOUNDS

No.	Compound	No.	Compound
1	Acetoin acetate	13	Isopentyl benzoate
2	2-Pentyl butanoate	14	Cinnamyl acetate
3	2-Nonanoate	15	Hexyl benzoate
4	Methyl benzyl ketone	16	Benzyl benzoate
5	Isopentyl pentanoate	17	Ethyl hexanoate
6	3-Phenylpropanal	18	Hexyl acetate
7	2-Phenylethyl acetate	19	2,5-Dimethyl-4-methoxy-2(2H)-furanone
8	Propyl benzoate	20	α -Terpinol
9	Ethyl nonanoate	21	<i>trans</i> -Cinnamaldehyde
10	Isobutyl benzoate	22	Eugenol
11	Hexyl hexanoate	23	Methyl cinnamate
12	Methyleugenol	24	α -Ionone
		25	β -Ionone

pounds in the sample being analysed by just looking at the chromatogram. The compounds can then be determined more accurately by using a slower programming rate. The principle of the calibration channel method and an example of using different programming rates with three model compounds are demonstrated in Fig.4; the retention indices are listed in Table I.

The choice of detector type best suited for a certain application depends on the elemental composition and electron affinity of the target compounds. A combined detection system with FID for analytical detection and ATD for calibration detection, is useful for samples that do not contain nitrogen or phosphorus (*e.g.* hydrocarbons, aroma compounds, fatty acids, polyhalogenated environmental contaminants) (Figs. 5 and 6, Table II).

An FID-ECD combination, with ECD for analytical detection, is useful for samples that do not contain compounds with high electron affinity. An ECD-ATD combination, with ECD for analytical detection, is very useful for the analysis of trace amounts of environmental pollutants with high electron affinity. Nitrogen and phosphorus compounds can be analysed with the ECD-ATD combination by using ECD for calibration detection. The retention index standards used in the last case must have a high electron affinity but no phosphorus or nitrogen atoms. Results of these experiments will be published elsewhere.

REFERENCES

- 1 A. Hesso and H. Piispanen, *Kem. Kemi*, 6 (1979) 12.
- 2 J. Enqvist and A. Hesso, *Kem. Kemi*, 9 (1982) 179 (Original in Finnish; English translation available).
- 3 J. Enqvist, A. Hesso, E. Rahkamaa, H. Björk, H. Piispanen, K. Siivinen, H. Kenttämää, A. Sivonen and E. Ali-Mattila, *Identification of Potential Organophosphorus Warfare Agents*, Ministry for Foreign Affairs of Finland, Helsinki, 1979, 1-200.
- 4 L. Koskinen, P. Sunila and P. Savolahti in *Trace Analysis of Chemical Warfare Agents, Part 1. An approach to the Environmental Monitoring of Nerve Agents*. Ministry for Foreign Affairs of Finland, Helsinki, 1981, p. 79.
- 5 K. Grob, *High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 493.