Journal of Chromatography, 472 (1989) 93–127
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 435

REVIEW

RECENT DEVELOPMENTS IN THE GAS CHROMATOGRAPHIC RETENTION INDEX SCHEME[a]

M. B. EVANS*
Division of Chemical Sciences, Hatfield Polytechnic, College Lane, Hatfield, Hertfordshire AL10 9AE (U.K.)
and
J. K. HAKEN
Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, NSW 2033 (Australia)

(First received November 18th, 1988; revised manuscript received February 22nd, 1989)

CONTENTS

1. INTRODUCTION

The specification of retention in gas chromatography in terms of the retention index[1], or, as it is frequently known after its founder, the Kováts retention index, has found universal application.

The index, first reported in 1958[1], found little acceptance during its first decade

---

[a] This work is dedicated to Professor E. sz. Kováts on the occasion of the 30th anniversary of the introduction of his retention index.

due to its publication in German at a time when the major advances in gas chromatography were occurring in the U.K. and the U.S.A.

Despite some limitations the index has found much greater usage than all other specialised retention specification schemes, the only specialized indices of particular importance being the carbon number[2] or equivalent chain length scheme[3] developed at about the same time and used extensively with lipids and the steroid number representation used with steroidal materials[4,5].

A major impetus to the exploitation of the index scheme occurred in the U.S.A. during 1964 when at the *Second International Symposium on Advances in Gas Chromatography* at Houston both Kováts and Keulemans[6] described aspects of the retention parameter. Much of the credit for the general acceptance of the index is, however, due to the efforts of Ettre[7], who summarized in English the papers previously published in German and included details of some related schemes in a work which formed the leading article in the issue of *Analytical Chemistry* that contained the symposium proceedings.

The index has been the subject of several substantive reviews[8–10] and then of a major one by Budahegyi *et al.*[11] published in 1983 to commemorate its 25th anniversary. This exhaustive work indicated that use of the index had been reported in about 1500 publications. Many of the reports were essentially compilations of retention data whilst others related the retention index of a particular class of compounds to a wide variety of physiochemical properties. In recent years a number of minor foreign-language reviews have appeared[12–17].

The present work is much more selective than that of Budahegyi *et al.*[11] and seeks generally to include the important aspects of the index and to indicate the developments that have occurred in the last five years.

It is clear that all of the correlations of retention indices and the various physico-chemical properties are of relatively short order, or with application being restricted to a particular functional class of functional classes.

Despite much work and many reports it is obvious that no realistic scheme of wide applicability is available for the precalculation of retention indices. This problem is highlighted by several factors. Many reports employ squalane or other low-polarity stationary phases where dispersion rather than polar interactions predominate and analyte adsorption at the liquid–solid interface, a recurrent problem, occurs. With polar stationary phases many of the correlations are simply not applicable.

With the availability of computers it is frequently not too difficult to produce a mathematical relationship or equation to relate a number of experimentally determined data points. With additional data, *i.e.*, more compounds, a new relationship or one with new values for the constants is necessary. Such relationships have continued to appear and these where they contain retention data are shown in the present work in the tabulation of retention indices. Reports of an analytical nature containing retention indices of isolated compounds are generally excluded.

The effects of temperature on retention was recognized early in the history of gas chromatography and increasing the temperature during the elution sequence was soon exploited in the examination of samples with wide ranges of boiling points. With linearly increasing column temperature a nearly arithmetic rather than a logarithmic relationship, as with isothermal conditions between retention and carbon number of homologues, was evident. To facilitate retention specification with temperature-programmed operation Van den Dool and Kratz[18] developed a programmed retention index (I_{TPGC}) using an arithmetic relationship similar to the logarithmic one of Kováts[1]. While this type of index is fundamentally different from that obtained isothermally, it has been the subject of much study due to the analytical importance of temperature programming, particularly with capillary columns. For this reason the development has continued to receive much attention and a variety of modified relationships have appeared in recent years.

As some difficulties have been experienced with the use of *n*-alkane standards, particularly with polar stationary phases, their appropriateness as standards has been questioned and a number of alternative reference series have been proposed.

Similarly, alternatives have been used with certain of the specific detectors where the alkanes do not give satisfactory responses. One situation which has received significant attention is the effect of adsorption on retention and in turn the retention index.

Other index schemes have been proposed, and both alternative standards and alternative index schemes are described in this work, neither of these areas having been described earlier by Budahegyi *et al.*[11].

In common with other areas of chromatography, it is evident that many reports, particularly from countries developing in chromatography, simply repeat results reported elsewhere years ago. Such works are generally not included in this work.

2. DEVELOPMENT OF THE RETENTION INDEX SYSTEM

The retention index (I) expresses the retention of a compound relative to homologous *n*-alkanes examined under the same isothermal experimental conditions. The retention index of a particular compound is defined as the carbon number multiplied by 100 of a hypothetical *n*-alkane having exactly the same retention characteristics, *i.e.*, adjusted or net retention time or volume or specific retention volume of the compound of interest measured under identical conditions[1].

The basic equation, first reported by Kováts and shown in eqn. 1, is based on the net retention of *n*-alkanes with an even number of carbon atoms.

$$I_S^{s.s}(T°C) = 200\,\frac{\log X_S - \log X_Z}{\log X_{(Z+2)} - \log X_Z} + 100Z \tag{1}$$

where I = retention index;

S = the compound of interest;

$Z, Z+2$ = *n*-alkanes with Z and $Z+2$ carbon atoms, respectively, where Z is an even number;

X = net retention value of substance and standards used;

s.s = stationary phase used.

In fact, the values of some physical constants, *i.e.*, melting points, spectroscopic data, alternate with the odd/even series. However, soon it was realised that this is not the case for solution data, and the derivation shown in eqn. 2 was proposed[8].

$$I_s(T°C) = 100\,\frac{\log X_S - \log X_Z}{\log X_{(Z+1)} - \log X_Z} + 100Z \tag{2}$$

Condition $X_Z < X_S < X_{(Z+1)}$

Subsequently, the more general expression shown in eqn. 3 was recommended by a working party of the Chromatographic Society[19].

$$I = 100N + 100n \frac{\log R_x - \log R_N}{\log R_{N+n} - \log R_N} \tag{3}$$

where R_x, R_N and R_{N+n} are the adjusted retentions of the analyte and *n*-alkane internal standards possessing N and $N+n$ carbon atoms, respectively. In general, eqn. 3 is a good approximation.

Both expressions are based upon the relationship between adjusted retention and carbon number for members of a homologous series of compounds shown in eqn. 4.

$$\log R = a + bN \tag{4}$$

The slope of the *n*-alkane log plot b, given by eqn. 5, which is determined by stationary phase polarity and mean column temperature, gives an immediate check on operating conditions[20].

$$b = \frac{\log R_{N+n} - \log R_N}{n} \tag{5}$$

For completeness the retention index should include the stationary phase used (s.s), the name of the compound of interest (S) and the temperature (°C) as shown in eqn. 1, but in practice these qualifications are rarely expressed in this way.

Kováts[1] originally suggested that three values be given: (i) the retention index at the column temperature; (ii) the retention index increment per 10°C; and (iii) the temperature range in which the index has been examined. The retention index values are directly proportional to the column temperature and with narrow temperature ranges ($\Delta T \approx 80$ K) are approximately linear although for wide temperature ranges ($\Delta T = 100$ K) the function is hyperbolic. Actually the validity of this statement depends largely on the precision of the determination.

The works of Kováts produced seven rules or relationships concerning retention index and chemical structure which also summarized regularities observed by other workers.

The first four propositions concerned the measurement of the retention index on a single phase while the remaining propositions concerned the measurement of the retention index of a particular solute on different stationary phases.

The propositions as discussed below all have been shown to be approximately true being considerable over-simplification of the actual behaviour.

(1) Within a homologous series the retention index of a higher homologue increases by 100 for each methylene unit introduced[1,21,22]. Exceptions were soon reported by Zulaica and Guiochon[23,24] who established considerably lower increments with dibasic esters. Subsequently it has been shown that few series increase by 100 units per methylene group but that most approximate to this value, *i.e.*, ± 10–15%.

The particular situation with alkyl esters has been extensively studied[25] and detailed in an earlier review[9], where it was apparent that the incremental increases varied widely. For the increments to be standardized retention plots of the homologous series must have the same slope or b value, *i.e.*, be parallel, and this does not occur.

(2) The relationship between the retention index of isomers and their boiling points was established. The differences in boiling points and retention indices of two isomers on a non-polar stationary phase such as a pure *n*-alkane or mixture of *n*-alkanes being shown by eqn. 6.

$$\mathrm{d}I = 5\mathrm{d}T_{\mathrm{B}} \tag{6}$$

where $\mathrm{d}I$ and $\mathrm{d}T_{\mathrm{B}}$ are the differences in the retention indices and the boiling points of the two isomers respectively[1,21,22]. A more complex relationship was subsequently reported between the retention index and the boiling point index by Matukuma[26] as shown in eqn. 7.

$$I_{\mathrm{B}} = 10^{(0.001340527T_{\mathrm{B}}+2.558916)} - 440.5 \tag{7}$$

where I_{B} is the boiling point index in retention index units and T_{B} is the boiling point (K at 101.25 kPa).

(3) The retention index of asymmetrically substituted compounds could be calculated from the retention index values of their symmetrical counterparts[27].

(4) Similar substitution in compounds of similar structure resulted in the same retention index increase[28].

(5) The retention index of non-polar compounds (alkanes) remains almost constant for any type of stationary phase[1,21,29].

(6) The retention indices of any compound determined on various non-polar stationary phases are identical or very close to one another[1,21,22].

(7) If the retention index of a compound is determined on a polar and on a non-polar stationary phase, the difference in the retention index values, *i.e.*, ΔI, is characteristic of the structure of the compound. Furthermore, values for retention index may be calculated for a particular molecule predicted by summation of the individual increments pertaining to the various adjacent zones within that molecule[1,21,22].

The introduction of the retention index was soon followed by a number of conceptually similar representations and these, together with other indices using different calibration series for particular applications, are briefly outlined.

The theoretical nonane number or R_{x9} value was introduced by Evans and Smith[30–32] in 1960. The corrected retention of a compound was expressed relative to a computed retention for *n*-nonane. The linearity of the *n*-alkane plot was indicated together with the inter-relation of the values. The determination of retention type indices in two stages being seen at the time as something of an advantage but the scheme has found negligible acceptance.

The methylene unit scheme (MU), developed by Vandenheuvel and Horning[33] for use with biological materials, is essentially identical to the retention index scheme. A calibration line using *n*-docosane and *n*-tetracosane was used to give the methylene unit value which is merely the retention index divided by 100. The carbon number[2] and equivalent chain length (ECL) schemes[3] employ a calibration line of the homologous methyl *n*-alkanoates. The steroid number (SN) uses a two-point calibration line of the hydrocarbons androstane and cholestane both with steroidal structures and with steroid numbers of 19 and 27, respectively[4,5], these being the number of constituent carbon atoms.

The interconversion of methods of retention presentation has long been of interest. Nine common representations of retention have been considered by Guerin and Banks[34] in 1966 and the interrelationship of equivalent chain length and retention index values has reported by Ashes *et al.*[35]. It is, of course, obvious that the universal use of minicomputers and microprocessors facilitates the interconversion of retention data.

3. ALTERNATIVES TO THE *n*-ALKANES AS CALIBRATION SERIES

Soon after the introduction of the *n*-alkanes as calibration standards alternative reference series began to be reported and this has largely continued to the present time. Certain of the alternatives have been suggested because of theoretical difficulties with the use of hydrocarbons, such as with highly polar stationary phases. Others have been necessary due to the introduction of element-specific detectors where the response of the *n*-alkanes is unsatisfactory. Sorption effects on retention indices were observed by Vandenheuvel and Horning[4] and later by Lorenz and Rogers[36], the recommendation in both cases being that the polarity of the solvent and solute should be similar. Alternative homologous series would be acceptable and be interconvertible[8], particularly if there was no adsorption at the liquid–gas interface.

An early suggestion of Dymond and Kilburn[37] was a carbon number system based on the 2-alkanones. These materials were again suggested by Ackman[38] in 1972 at a time when Grobler[39] briefly outlined the limited practicability of retention indices. Grobler highlighted the low retention values of *n*-alkanes on polar stationary phases and argued that the gas chromatography of compounds of greatly different boiling points could not be performed favourably under strictly identical conditions. *n*-Alkanols were proposed as standards but were subsequently criticized by Hawkes[40] due to the well-known anomalous effects of the hydroxyl groups. Hawkes acknowledged the limitations of simple hydrocarbons and indicated the *n*-propyl ethers as the almost ideal standards. The ether groups are in a total methylene environment uncomplicated by the effects of terminal methyl groups and display weak orientation and proton acceptor Hildebrand parameters with an absence of proton donor effects. Furthermore they are readily synthesised from the corresponding *n*-alkanols. Other available series were indicated to be unsuitable for instance the highly polar *n*-alkanols, the alkanals which have low stability and are odorous and alkan-2-ones which are not favoured due to their Hildebrand parameters.

Lower and symmetrical alkanoate esters have been evaluated as reference series[22,41] and found to be more suitable with polar solvents than hydrocarbons as suggested by Vandenheuvel and Horning[4] and Lorenz and Rogers[36]. At the time it was indicated that it was unlikely that a single reference series would ever be universally acceptable, but the difficulties were in many cases decreasing due to improvements in systems of measurement, data processing and interconversion.

Nine homologous series of compounds were examined as reference standards by

Heldt and Köser[42] using the generalised retention index developed by Novák and Růžičková[43]. These included *n*-alkanes, *n*-alkenes, *n*-alkanals, 1-chloro-*n*-alkanes, *n*-alkan-1-ols, *n*-alkan-2-ols, 1-aminoalkanes, *n*-alkylbenzenes and *n*-alkylcyclohexanes. It was found, not unexpectedly, that alkenes behaved similarly to alkanes while *n*-alkanols were unsuitable with non-polar stationary phases. The aminoalkanes were found to be unsatisfactory and the chloroalkanes of limited use with highly polar stationary phases. The *n*-alkanals were preferred as standards despite their acknowledged problems reported earlier.

Of the compounds examined[42], alcohols[43,44], ketones[44,45], esters[44] and *n*-alkylbenzenes[46,47] had been previously reported. The use of *n*-alkylbenzenes as retention standards[47] has been reported to be unsatisfactory due to poor linearity of the calibration line, which was attributed to the relative contribution of the aromatic nucleus and the methylene chain.

When stationary phases are ranked in a polarity scale, it is apparent that the particular reference standards are of major importance. With the usual situations the retention of the *n*-alkane standard largely determines the ranking. This was established 25 years ago by Littlewood[48] and was subsequently reiterated by Ashes and Haken[4] and Aue and Paramasigamani[49].

With the introduction of specialised and element-specific detectors further impetus was directed towards suitable reference standards. An early report of standards for use with electron-capture detectors was that of the *n*-alkyl iodides by Castello *et al.*[50] in 1969. With nitrogen–phosphorus specific detection a serious problem arises as the *n*-alkanes are virtually non-detectable. Attempts at overcoming the problem have included (a) the use of excessive injection of *n*-alkanes to achieve a slightly greater response[56], (b) the use of a mixture of nitrogen-containing compounds (frequently drugs) as secondary standards with published retention index values instead of the *n*-alkanes[51] or (c) use of relative retention times based on nitrogen-containing drugs as internal standards instead of the Kováts procedure using *n*-alkanes[52,53].

The use of excessive amounts of *n*-alkanes with nitrogen–phosphorus detection can lead to variation of the retention time, peak broadening, peak tailing and peak splitting[54].

A method developed by Asselin[55] allows the detection of compounds such as the *n*-alkanes which do not contain phosphorus or nitrogen using a thermionic phosphorus–nitrogen specific detector. The method requires the temporary conversion of the nitrogen–phosphorus detector into a detector with properties approximating those of a flame ionization detector. The hydrogen flow-rate was deliberately increased from its normal flow-rate (2.0–4.0 ml/min) to 8 ml/min where the *n*-alkanes are readily detected. After this calibration has been achieved the gas flow-rate is returned to its normal level to allow nitrogen–phosphorus detection. A reconditioning period of about 45 min is necessary to ensure that the ceramic bead of the detector is sufficiently stable for quantitative measurements.

During the 1980s there has been a very large number of alternative reference series proposed for use with the electron-capture and specific-element detectors particularly for nitrogen, phosphorus- and halogen-containing materials, drugs, polychlorinated biphenyls and other aromatic compounds, which have become of considerable importance.

The symmetrical *n*-dialkyl (C_{4-12}) sulphides were examined by Zotov *et al.*[56] for use with detectors insensitive to *n*-alkanes. Retention indices (I_S) were obtained isothermally and also by temperature programming using the equation of Van den Dool and Kratz[18]. It was reported that the dialkyl sulphides follow the same laws as the *n*-alkanes and are satisfactory as standards.

A multidetection retention index scheme has been developed by Enqvist *et al.*[57] involving the use of *n*-alkyl bis(trifluoromethyl)-thiophosphinates as internal standards in connection with element-specific assays. The multifunctional standards enable the measurement of a form of retention index with single or dual-channel instruments equipped with flame ionization, electron-capture, nitrogen–phosphorus and flame photometric detectors. With the latter of single-column instruments equipped with an appropriate effluent stream splitter, the combination of element-specific and flame ionization detection can yield conventional retention indices by the conversion of relative retention ratios by means of the expression[58] shown in eqn. 8.

$$I = 100\,\frac{\log R_{xS}}{b} + I_S \qquad (8)$$

where R_{xS} is the retention of the unknown relative to the multifunctional standard, obtained by element-specific detection, and I_S is the retention index of the *n*-alkyl bis(trifluoromethyl)thiophosphinate standard obtained by flame ionization detection.

The *n*-alkyl trichloroacetates were described as retention index standards by Neu *et al.*[59] in 1978 who also reported their use in several works concerning the analysis of polychlorobenzenes and polychlorinated biphenyls[60,61].

Analysis of polychlorinated biphenyls was also carried out using *n*-alkyl trichloroacetates as standards by Schwartz *et al.*[62]. Three esters were used, namely the *n*-decyl, *n*-dodecyl and *n*-pentadecyl. A computer-assisted technique for the quantitative determination of many of the 209 theoretically possible polychlorinated biphenyl isomers was subsequently described by the same workers[63]. The *n*-C_{8-20} alkyl trichloroacetates were used as external retention standards by Wegman and Hofstee[64] for analysis of polychlorinated biphenyls in aquatic sediments using temperature programming.

A method for the calculation of retention indices using a power series expansion of the logarithmic relationship between retention and carbon number was reported by Heeg and Zinburg[65]. The trichloroacetates were indicated to be a suitable reference series for compounds sensitive to electron-capture detection.

The monobromoalkanes have continued to be recommended as retention calibration markers[44,50,66] for use in both the isothermal and temperature-programmed mode.

The retention index shown as I' of 221 halogenated aliphatic and alicyclic compounds have been reported on the 1-bromoalkane scale by temperature-programmed capillary gas chromatography by Yasukara *et al.*[66] while elemental iodine was determined with electron-capture detection using retention indices based on *n*-alkanes and alkyl iodides. The iodine passed through the column without conversion to an organic halide with concentrations of 118 mg/ml being determined[67].

Pacholec and Poole[68–70] used a homologous series of *n*-bromoalkanes to produce a retention index scale and a novel calibration method for use with electron-capture detection. The response per mole of the detector is identical for all the

C_{5-18} *n*-bromoalkanes. An internal calibration curve was obtained for each sample injected by adding several *n*-bromoalkanes the molar concentrations of which are related in a simple step wise fashion to one another. This calibration method is capable of a relative average percentage error of 4–10% compared with an error of 12–20% with the standard calibration method for concentrations above the detection limit. The method with *n*-alkyl iodides[70] was applied to temperature-programmed capillary gas chromatography. Retention indices were reported to be reproduced with an average standard deviation of approximately 0.35 index units with the relative error for the method being similar to that achieved by daily solute calibration.

A chromatographic retention index (I_N) based on homologous tri-*n*-alkylamines has been devised for use in the detection of pesticides and related compounds in body fluids of agricultural workers[63]. The amines tri-*n*-propylamine and tri-*n*-decylamine were assigned index values of 300 and 1000 according to the number of carbon atoms in a single alkyl chain. Capillary column studies using dimethyl polysiloxane produced index values for 106 pesticides and related compounds. The relationship between these indices and those of Kováts was examined[71]. A subsequent capillary column study[72] of 152 drugs and metabolites was carried out using 5 and 50% phenyl-substituted polysiloxane as stationary phases. The retention indices were obtained by increasing the hydrogen and air flow-rates essentially as indicated by Asselin[55].

An index system suitable for electron-capture detection in the examination of pesticides and environmental compounds by temperature-programmed capillary gas chromatography has been developed using chlorinated compounds such as chlorobenzene isomers and decachlorobiphenyl. The scheme described as the chlorophenyl (CP) index used 1,3,5-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene and decachlorobiphenyl as standards with assigned values of 300, 400, 600 and 1000, respectively[73].

Nakamura[74] has examined, with environmental samples, sulphur-containing heterocyclic compounds and compared the polyaromatic hydrocarbon (PAH) index, the retention index and the CP index.

Polychlorinated biphenyls have been obtained for use as retention index standards by the partial catalytic dechlorination of polychlorinated biphenyls having up to six chlorine atoms. The dechlorination employed $NaBH_4$ and $NiCl_2$ catalysts generated *in situ*, and all the expected polychlorinated biphenyl congeners were observed[75].

A study of the retention indices of PAHs on a low-polarity capillary column (SE-52) showed poor statistical reliability. A new retention index described variously as the PAC index, the PAH index or the Lee index was developed based on a series of PAHs[76].

The standards naphthalene, phenanthene, chrysene and picene were assigned values of 200, 300, 400 and 500, respectively, with the system having no foundation in chromatographic thermodynamics. It does not assume a linear relationship between retention and ring number or other structural parameters and uses the linear equation of Van den Dool and Kratz[18].

The retention indices of more than 200 PAHs were determined with the average 95% confidence limits for four determinations on each PAH being ±0.25 index units[76]. A subsequent work[77] evaluated the results of 29 routine capillary gas chromatographic analyses of complex mixtures of polyaromatic compounds. The temperature-programming rates and the effect of initial isothermal periods were examined and tabulations of additional polyaromatic compounds, including 78 hydrocarbons, 115 sulphur and 117 nitrogen heterocyclic compounds included.

The PAH index has been applied to a considerable number of related studies of: diesel particulate matter[77,78], coal extracts[79], synthetic fuels[80,81], tissues and sediments[82–85], air particulate matter[86] and combustion effluents[87].

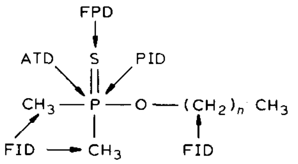
Rostad and Pereira[88], using gas chromatography–mass spectrometry of environmental samples, determined PAH indices and modified Kováts indices (I_{TPGC}) for a wide range of aromatic and aliphatic compounds.

The PAH index system has been applied to an automated system for the analysis of products generated by coal gasification in a two-stage fixed-bed gasifier system[89]. A similar system using both gas chromatography and gas chromatography–mass spectrometry for the same application has been reported by Stamouis and Demirgian[90].

Several specialised series of compounds have been synthesized for application with the newer specific detectors.

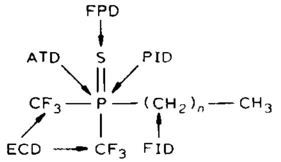
A homologous series of 2,4-dichlorobenzyl alkyl ethers (C_{2-16}) was synthesized and purified for use as retention index standards. The compounds are stable, sensitive to electron-capture and flame ionization detection and suitable for gas chromatography–mass spectrometry with base peaks of m/z 159/161. On fragmentation good total ion current detection occurs with an intense ion at an $m/z > 100$ above the low mass background with suitability for single or multiple ion monitoring[91,92].

Of two related series the first described as the P series by Manninen *et al.*[93] are alkyl dimethylphosphinothioates, which possess functional groups suitable for use with flame ionization, nitrogen–phosphorus and flame photometric detection, but not electron-capture detection.



ATD = alkaline thermoionization detection
FPD = flame photometric detection
FID = flame ionization detection
PID = photoionization detector

Subsequently, a series of alkyl bis(trifluoromethyl)phosphinesulphides were introduced (designated the M series) that are suitable also for use with electron-capture detection[94].



ECD = electron-capture detection

The components of the M series were detected at the level of 0.4–0.6 pmol with flame ionization detection, 2–7 fmol with nitrogen–phosphorus detection and 305 fmol with electron-capture detection. The sensitivities of nitrogen–phosphorus and electron-capture detection are so much greater than flame ionization detection that their parallel use with the two-channel chromatograph was not possible.

The components of the M series are comparatively non-polar on the non-polar (SE-54) stationary phase and differ little from those of the *n*-alkanes. A linear correlation was shown between the retention indices of nine different chemical agents based on the *n*-alkanes and the M series. The M series standards also have been used in a multidetector system[57].

It is clear that while a considerable number of homologous series have been reported as retention standards there is little likelihood of a universally acceptable series ever being established. With many of the specialised series higher homologues are involved than with the *n*-alkanes. In these cases, *i.e.*, fatty acids, the difficulties of deviation from linearity of the lower members in the semi-logarithmic plot of retention and carbon number are not experienced.

4. LOGARITHMIC INDEX SCHEMES

A number of index schemes very similar to the retention index have been reported and are described below.

Considering the thermodynamic derivation of the retention index Heeg and Zinburg[65] have shown, as have many other workers, that the linear relationship between the logarithm of the net retention time and the carbon number of homologous series is valid only to the first approximation. The authors reported that with accurately measured solute values a more exact description of their function is achieved by the use of a power series of higher order as shown in eqn. 9.

$$\log t'_R = \alpha + \beta c + \gamma c^2 + \delta c^3 + \ldots \tag{9}$$

where t'_R is the adjusted retention time, c is the carbon number and α, β, γ, δ, etc. are constants. These considerations led to a method for the determination of retention indices which by virtue of the more vigourous treatment are reported to make possible extrapolation over a wider range and similarly wider interpolation.

4.1. Generalised retention index

The generalised retention index $I_y^x(i)$ was developed by Novák and Růžičková[43] in 1974 and is a simple extension of the Kováts index which allowed the retention index to be applied to other homologous series of standards. The index is shown in eqn. 10.

$$I_y^x(i) = \frac{100(\log V^x_{N(i)} - \log V^x_{N(yn)})}{\log V^x_{N(yn+a)} - \log V^x_{N(yn)}} + 100_n + Ky \tag{10}$$

where $V^x_{N(i)}$, $V^x_{N(yn)}$ and $V^x_{N(yn+a)}$ are the net retention values on a stationary phase x of the substance examined, and of the reference compound with N, and $(N+a)$ methylene units, respectively. Ky is a constant selected to avoid negative indices where with *n*-alkanes $Ky = 0$.

The scheme was subsequently evaluated by Heldt and Köser[42] using nine homologous series of varying functional class, most of which had been considered previously by other workers.

The same name, *i.e.*, generalized retention index, has been given to a scheme by Zenkevich[95]. A new algorithm for calculating retention indices is based on a linear relationship between I and $(t'_R + q \log t'_R)$ where t'_R is the adjusted retention time and q is a coefficient related to the analytical conditions. The generalized retention index values combine the system of logarithmic Kováts indices and linear indices. The generalized retention index under any conditions of temperature programming can be compared with the normally isothermally determined Kováts index.

The Kováts equation as shown in eqn. 11 is a logarithmic relationship of retention and carbon number.

$$\log R = a + bN \tag{11}$$

The linear equation of Van den Dool and Kratz[18] may be shown as

$$R = a' + b'N \tag{12}$$

where N is carbon number and a, a', b and b' are constants.

4.2. *Homologous index*

The same idea as the generalised retention index termed the homologous index (I_h) has recently been described by Luo *et al.*[14]. This is defined as a retention index obtained by using the homologous series of the substance to be characterized by gas chromatography as the reference series. Based on the analysis of hierarchial data with five sources of variation, the relative standard deviations of the proposed homologous retention index caused by the concentration of stationary phase and column temperature are much smaller than those of relative retention and Kováts retention indices. The homologous retention index is claimed to be more precise and reliable for characterization. The retention index is considered to be a special case of the homologous retention index when the *n*-alkanes are used as standards.

The conclusions of the authors that it is preferable to use standard similar to the compounds examined are as previously reported by other workers, both with regard to the characterization of solutes and solvents.

4.3. *Unified retention index*

The unified retention index developed by Dimov[96] has been used to explain the variations in the retention index of simple hydrocarbons on squalane which are largely attributed to random errors. The temperature dependence of retention index is well known, the function $\mathrm{d}I/\mathrm{d}T$ being hyperbolic. A statistical treatment using simple regression analysis of the data allows computation of a unified retention index (UI_T) as shown in eqn. 13.

$$UI_T = UI_0 + (\mathrm{d}UI/\mathrm{d}T)T \tag{13}$$

where UI_0 is the value of UI_T at 0°C and $\mathrm{d}UI/\mathrm{d}T$ the temperature dependence where $-\mathrm{d}UI/\mathrm{d}T$ is the slope of the plotted data.

Tabulated data were presented for many hydrocarbons on a squalane column[96] and subsequently on dimethylpolysiloxane (OV-101) between 40° and 70°C[97] and later for aromatic hydrocarbons on squalane[98]. An algorithm has been reported for the precalculation of the optimum separation for the gas chromatography of a petroleum fraction. The algorithm is based on two concepts, the unified retention index and a mathematical description of the dependence of the peak width and retention indices and on the column temperature[99].

The retention of the hydrocarbons present in the C_5 pyrolysis fraction of gasolines on squalane and dimethylpolysiloxane oil (J × R) capillary columns was investigated. The unified retention indices of the hydrocarbons were determined on squalane. The retention indices obtained on the two phases were interrelated. Equations based on the unified retention indices on squalane allowed calculation of the values on dimethylpolysiloxane with reasonable accuracy[100].

4.4. *Standard retention index*

Robinson and Odell[101] in 1971 proposed the standard retention index scheme I_{STD} using the equation developed by Kováts[1] but considering the boiling points of the substances as shown in eqn. 14.

$$I_{\mathrm{STD}} = 100n + 100\,\frac{\log BP_x - \log BP_n}{\log BP_{n+1} - \log BP_n} \tag{14}$$

where BP_x, BP_n and BP_{n+1} are the boiling points of the compound of interest and of the n-alkanes with n and $n+1$ carbon atoms respectively. A standard retention index difference (ΔI^*) was obtained by comparison of the standard and experimental retention indices.

$$\Delta I^* = I_{\mathrm{STD}} - I_{\mathrm{x}}^T$$

where I_{x}^T is the retention index of the compound at temperature T on the stationary phase x. The method has found no acceptance and Dimov[102] in an evaluation found the accuracy to be low.

4.5. *Invariant retention index*

The effect of the solid support on the chromatographic separation has long been realised especially by Berezkin[103,104], who developed the relationships shown in eqns. 15–17.

$$I = I_0 + a/P_{\mathrm{L}} \tag{15}$$

$$I = I_0 + b/k_{\mathrm{s}} \tag{16}$$

$$I = I_0 + c/V_{\mathrm{L}} \tag{17}$$

where I_0 is the invariant retention index;
a, b and c are constants;
P_{L} is the percentage stationary phase on the solid support;
V_{L} is stationary phase volume in column;
k_{s} is the capacity factor for the reference compound, the retention of which is mainly determined by its solubility in the stationary phase.

It was found preferable[105] to use the equation containing the capacity factor, as the equation with the stationary phase loading is of low precision due to its measurement with losses that are experienced during coating. Similarly, the relationship with the capacity factor allows calculation of the invariant retention indices on capillary columns with small errors[106,107].

The invariant indices based on the *n*-alkanes, *n*-alkan-1-ols and *n*-alkan-1-ol acetates were reported for insect sex pheromones and their structural analogues belonging to a series of saturated and unsaturated alcohols and esters. The homologous series of alkanols and esters were found to be the most suitable standards for determinations with the minimum errors.

The interlaboratory reproducibility of gas chromatographic data was reported to be improved by determination of invariant indices. Studies were carried out using squalane for the separation of hydrocarbon mixtures to demonstrate the difference between conventional and invariant retention indices[108].

A linear relationship between retention indices and the film thickness of the stationary phase (PEG 20M) in capillary columns was reported[109].

The use of the invariant indices in the calculations increased the reproducibility in the determination of the retention indices when different operators and different laboratories were involved. The invariant index is reported to be independent of the column packing material.

4.6. *Universal retention index*

It has been reported by Belyaev and Vigdergauz[110] that the reference solutes should not be identical in chemical nature, for instance as with the *n*-alkanes, but rather identical with respect to the degree of sorption on different stationary phases, *i.e.*, hypothetical compounds with fixed values of the distribution coefficient (or retention volume) which do not alter when going to different phases.

Values of selectivity coefficients equal to the ratio of the reduced retention times of neighbouring homologues on non-polar stationary phases near 100°C where the polarity factor N_u is approximately 2. It is proposed that the universal series be a hypothetical reference series where retention is determined from the relationship shown in eqn. 18.

$$V_{g(N)} = 2^{N-1} \tag{18}$$

Where $V_{g(N)}$ is the absolute specific retention volume of N, the hypothetical compound, the first member of the series being assigned $V_g = 1\ \mathrm{cm^3/g}$ (close to V_g of methane on non-polar phases at 100°C).

The retention of each subsequent member will be twice as great as the preceeding one hence the reduced retention time (t'_{RN}) of the hypothetical reference compound, NH, is given by the expression shown in eqn. 19.

$$t'_{RN} = \frac{2^{N-1} gT}{FJ \cdot 273.15} \tag{19}$$

where g is mass of stationary phase (g);
T is column temperature (°C);
F is flow-rate (ml/min);
J is pressure gradient factor.

A comparison of nine methods for determining the universal retention index has recently been reported by Belyaev and Vigdergauz[111] using both experimentally determined and published retention data. The valuations were carried out using alkanes, alcohols and aromatic hydrocarbons. Chromatography was performed at 120°C using a liquid crystal stationary phase (*p*,*p*′-ethoxypropoxyazobenzene).

4.7. *Molecular retention index*

The molecular retention index (ΔM_e) was developed by Evans and Smith[112,113] in 1961 as an alternative to the retention index. The index is similar to the Kováts scheme[1] and is defined as the molecular weight of a hypothetical *n*-alkane having the same retention as the compound under study. The formula of the hypothetical *n*-alkane equivalent to the compound is $C_{I'}H_{2I'+2}$ and will have an effective molecular weight given by the relationships shown in eqns. 20 and 21.

$$M_e = 14.026\ I' + 2.016 \qquad (20)$$

$$= 0.1406\ I + 2.016 \qquad (21)$$

where $I = 100\ I'$;
M_e = effective molecular weight of the solute or the molecular weight of a hypothetical *n*-alkane with I' carbon atoms;
I' = number of carbon atoms in the hypothetical alkane;
$\Delta M_e = M_e - M$;
M = the actual molecular weight.

The difference between the effective and true molecular weights of the compound were suggested to be a useful parameter for the correlation of chromatographic retention and chemical structure.

The scheme was subsequently developed by Evans[114] and has been suggested for stationary phase characterization without the necessity for using the unstable squalane base stationary phase[115,116].

The scheme has found negligible acceptance, nevertheless such relationships have subsequently been reported by several workers. Piringer *et al.*[117] in 1976 described a method in which combinations of retention increments, compatible with the empirical formula and the retention of an unknown compound are used for its identification.

A parameter W was determined as shown in eqn. 22.

$$W = M_e - M \qquad (22)$$

$$= 0.14I - M + 2$$

where M = molecular weight;
M_e = molecular retention index;
I = retention index.

More recently a similar scheme has been detailed by Zenkevich and Malamakhov[118] in 1987; however, in common with the previous molecular retention index systems it has found little application.

4.8. Dispersion and selectivity indices

While it has been considered that the molecular retention index (ΔM_e)[112,113] has some advantages over the retention index for the characterization of both solvents and solutes, it has not found acceptance. Accordingly a scheme was developed[119] whereby the retention index and molecular retention relationships were combined hopefully to extend the utility of the almost universally used retention indices.

For a particular solute the partition coefficient is determined by the magnitude of the intermolecular forces involved in its interaction with the stationary phase. With *n*-alkanes these forces are almost exclusively London dispersion forces, which are additive and increase with molecular weight. As heteroatoms and multiple bonds are introduced into a molecule, polar forces contribute increasingly to the overall retention. It is these forces, moderated by the influence of molecular shape or steric effects, that account for selectivity.

On the assumption that the non-polar forces involved in retention are directly proportional to the molecular weight, the retention index may be shown by eqn. 23.

$$I = I_M + I^* \tag{23}$$

where the dispersion index I_M is defined as the retention index of a hypothetical *n*-alkane having the same molecular weight as the solute; I^* = selectivity index; and I = retention index.

When I_M is defined as in eqn. 23 its value may be determined according to the relationship shown in eqn. 24.

$$I_M = \frac{M - 2.016}{0.14026} \tag{24}$$

where M = molecular weight. The retention index $I = 100i$ where i is the carbon number of hypothetical *n*-alkane C_iH_{2i+2} or $(CH_2)_i + 2H$, with a molecular weight of $14.026i + 2.016$. By definition $I_M = I$ for *n*-alkanes, the difference I^* of the solute reflecting the combined polar interaction.

The selectivity index I^* is the carbon number equivalent of ΔM_e given in eqn. 25.

$$\Delta M_e = M_e - M \tag{25}$$

where M_e = molecular retention index arising from the logarithmic relationship between the retention of the *n*-alkanes and molecular weight.

M = molecular weight of the particular solute.

It has been shown that solutes possessing polar functional groups tend towards positive I^* values whereas chain branching and substituents with screened electrons yield negative values.

The scheme has recently been demonstrated using a large number of homologous series of halogenated cyclic compounds[120], alkyl- and alkenylbenzenes[121], aliphatic[122] and aromatic[123] esters and halogenated aromatic compounds[124] and also for stationary phase characterisation[125].

A similar concept recently has been applied to liquid chromatography by Yamaguchi and Hanai[126]. The retention of a molecule in high-performance liquid chromatography was considered to be determined by various intermolecular interactions, dispersion, inductive, orientative and charge-transfer including hydrogen bonding. Dispersive, inductive and orientative interactions additively can be related to molecular size (Van der Waals volume). On the other hand, the selectivity of retention difference may be related to charge-transfer interactions, including hydrogen bonding. The equation proposed by Evans *et al.*[119] was modified to give eqn. 26.

$$R = R_v + R^* \tag{26}$$

where R_v, the molecular size index, is defined as the retention index of a hypothetical *n*-alkane having the same Van der Waals volume as the analyte and R^* is a selectivity index similar to the energy effect in reversed-phase liquid chromatography[127,128].

5. LINEAR INDICES

A simple linear index scheme (J) was reported by Vigdergauz and Martynov[129,130] using the uncorrected retention of the *n*-alkanes as a basis for interpolation according to eqn. 27.

$$J = \frac{d_{\text{substance}} - d_{n-c_Z}}{d_{n-c_{Z+1}} - d_{n-c_Z}} \tag{27}$$

Where $d_{\text{substance}}$, d_{n-c_Z} and $d_{n-c_{Z+1}}$ are the gross retention values of the substance and *n*-alkanes with Z and $Z+1$ carbon numbers, respectively. An identical relationship was introduced about the same time by Harbourn[131] who stressed the simplicity of its use, nevertheless the scheme has found little usage in isothermal gas chromatography[132,133]. It is evident that such uncorrected indices are of negligible interlaboratory use and have little theoretical basis in chromatographic thermodynamics. Such linear indices have found widespread use in temperature programmed gas chromatography. It was early recognised that with a linear temperature increase a near linear relationship existed between the retention of homologues and their carbon number. The equation of Van den Dool and Kratz[18] providing a temperature-programmed version of Kováts indices shown as I_{TPGC} was developed in 1963. And since this time with the extensive acceptance of temperature-programmed operation such linear indices have received much attention. Such indices, however, have little basis in theory and are found to be much more variable than isothermal results, particularly on an interlaboratory scale. The very many conflicting works that have appeared on the topic are not include here.

With programming of the carrier gas, *i.e.*, flow programming, very minor variations of the retention indices only are experienced; however, the technique while developed decades ago has found negligible acceptance.

6. DEAD TIME CONSIDERATIONS

The estimation of the dead time or gas hold-up time corresponding to the instrumental contribution to the gross retention is of considerable importance in the accurate determination of the retention of a compound, and similarly to any subsequently calculated retention index.

The major interest in dead time determination during the last decade has been its measurement mathematically. This is conveniently carried out by linearisation of the alkane calibration plot where a single injection of the homologous *n*-alkanes provides the dead time and the adjusted retention times of the *n*-alkanes for use in the determination of the retention index.

Because of the widespread use of on-line data processing the topic has been extensively studied and has been the subject of several reviews[134–136] and reports comparing the effectiveness of some of the principal procedures. These works have essentially included all the published work in the area and the details are not repeated here.

The use of linearisation of the *n*-alkane line depends on a linear relationship existing between carbon number and retention. This has been a contentious issue for years and it is now evident in most if not all cases that at least some minor deviations exist with the lower members of a homologous series[137]. A widely used procedure being to avoid the use of the lower homologues with the values being readily calculated mathematically. The area has also been examined by Riedo *et al.*[138] who showed that the relationship between the carbon number and logarithm of the net retention was not strictly linear. As an alternative they presented simple methods for the determination of the dead volume using flame ionisation and thermal conductivity detection.

While methane was unsatisfactory it does not give a value near the true zero. The true zero was determined from the relative retentions of a pair of substances determined with the necessary precision. Methane was one substance selected and was injected together with a second compound A, which is sufficiently separated from methane. The relative retention of A with respect to methane is then given by eqn. 28:

$$r_{\mathrm{A/CH_4}} = \frac{X'_{\mathrm{R}}(\mathrm{A})}{X'_{\mathrm{R}}(\mathrm{CH_4})} = \frac{X_{\mathrm{R}}(\mathrm{A}) - X_{\mathrm{m}}}{X_{\mathrm{R}}(\mathrm{CH_4}) - X_{\mathrm{m}}} \tag{28}$$

where X is the retention property of the solute (distance, d; time, t; volume, V) and r_{A}, X_{R} and X_{m} represent the gross, corrected (net) and dead retention properties, respectively. Eqn. 28 gives, after the necessary transformations:

$$X_{\mathrm{m}} = X_{\mathrm{R}}(\mathrm{CH_4}) - \frac{X_{\mathrm{R}}(\mathrm{A}) - X_{\mathrm{R}}(\mathrm{CH_4})}{r_{\mathrm{A/CH_4}} - 1} = X_{\mathrm{R}}(\mathrm{CH_4}) - \delta \tag{29}$$

For calculation of the value of δ, a precise knowledge of the relative retention $r_{\mathrm{A/CH_4}}$ is necessary.

A chromatograph fitted with a thermal conductivity detector and a hydrocarbon ($C_{87}H_{176}$) column was used for determination of the gross retention volumes of a series of permanent gases and light hydrocarbons. The results showed neon to have the smallest gross retention time and thus accepted as the dead volume. With a thermal conductivity detector, nitrogen was accepted as a non-retained substance.

Various alternative homologous series have been used for the determination of the dead time. An early work considered C_{11-15} methyl *n*-ketones, C_{10-20} methyl *n*-alkanoates, C_{10-20} *n*-alkanols, and C_{12-24} *n*-alkanes where it was concluded that little difference was experienced with the various systems[139]. A more recent work[47], however, showed that the *n*-alkylbenzenes were unsuitable for the purpose of dead time calculation in gas chromatography.

The use of methane as void volume marker, first proposed by Feinland *et al.*[140], is frequently used in retention index measurements. However, although convenient the method is suspect because methane is known to be retained significantly on apolar columns at moderately high temperatures[141]. An observation which is at variance with Kováts' proposal that assumes a value of 100 for methane whilst as a valid dead time calibrant a value of zero is necessary.

Parcher and Johnson[142] also used inert gases to calculate the dead time and noted that methane did not fit on the linear semilogarithmic plot of retention and carbon number. They reported an effective carbon number of 0.5 for methane. A wider range of stationary phases was subsequently used[143] to investigate the effective carbon number as mathematically the deviations from linearity on a plot appeared small. Wide variations in the effective carbon number of methane were observed on the various phases but in all instances the values were substantially closer to unity than previously reported.

It is of course apparent that the effect of variations in the determination of dead line are more serious with compounds of lower retention however with the very widespread use of computerised systems the procedure adopted should be as rigid as possible. While the equations of Kováts were reported long before the use of computerised systems two problems have been observed in the mathematics involved. Alternative mathematical procedures have been discussed to remove these difficulties[144].

7. REPRODUCIBILITY OF RETENTION INDICES

Retention indices may be reproduced within a laboratory using modern instrumentation with considerable precision over finite time periods, *i.e.*, often short, depending on the stability of the stationary phase. Reproducibility of 0.05–0.1 units was reported by Schomberg and Dielmann[145] in 1973 and such results were routinely obtained in studies of McReynolds constants at about the same time. However, columns with sensitive packings such as the squalane standard produced reproducible results for only a few hours and therefore required to be continually replaced. For routine operation a reproducibility of about one index unit might be expected with a non-polar phase and 2–3, possibly 5, units with a highly polar phase.

Errors that occur in retention index determination may be random or systematic[145–148]. Random errors fall within two areas, namely errors in measurement of the elution time and variations in elution time that occur due to small alterations in the instrumental parameters, *i.e.*, oven temperature, gas flow. While elution time is now accurately measured and operating conditions are more closely controlled it is difficult to ensure that such errors are eliminated. The chromatographer has little control over such errors which are largely characteristic of the instrumentation used. Systematic errors are caused by many factors although the stability of the stationary phase is probably the most serious cause followed by solute adsorption at the solid–liquid interface. While some improvements in these areas are possibly by the chromatographer it has been suggested that it is not possible to ensure their complete elimination as no acceptable monitoring procedure is available[147].

The performance of a material as a stationary phase apart from a suitable physical form depends on its chemical nature, *i.e.*, chemical composition, and obviously to obtain reproducible results this must remain unchanged. Large numbers of reports over decades have appeared concerning the thermal stability and variability of composition of stationary phases and while improved products have been available in recent years, considerable further improvement is possible.

While attention has been directed to the stationary phase the packing of a conventional column or coating of a capillary column is equally of importance in influencing operation and achieving reproducible results. Many phases are susceptible to various solvents and care must be exercised from the commencement of preparation. With packed columns the inertness of the support is significant as is deactivation of the inner surface of capillary columns.

Many phases contain low-molecular-weight compounds which tend to bleed away in use and alter the chemical composition of the phase and accordingly its column characteristics. The majority of phases are polysiloxanes which usually contain small amounts of cyclic and linear oligomers or reactive intermediates, depending on the method of synthesis, as well as catalyst residues from the syntheses. With immobilised phases cross-linking catalyst residues frequently remain while with many early laboratory prepared columns the degree of cross-linking varied slightly with each column as indicated by the varying amounts of materials leached away by solvents. All of these compounds present in a phase are of slightly different polar character and effect the overall retention characteristics of the material. As all of these components are lost or vary in composition with column use the retention characteristics as a consequence continually drift. With the increasing use and availability of commercially prepared columns some of these difficulties are reduced.

Peak tailing is a fairly common phenomenon and is frequently due to adsorption of the solute on the support. With significant tailing the elution pattern is altered. In gas chromatography, separation and elution are due to a partition mechanism while adsorption introduces a second mechanism and accordingly a composite mechanism is in operation. Supports have been even more variable than stationary phases and the adsorption contribution to elution should be minimal to ensure reliable peak identifications.

Adsorption has been suggested as the principal cause of poor inter-laboratory reproducibility of retention data[149] the effect is most apparent with non-polar phases where the polar contribution of the phase is low and that of the support relatively high. The increased effect of adsorption with decreasing stationary phase film thickness having been demonstrated by Krupčik and co-workers[150–151].

8. GAS-LIQUID INTERFACIAL ADSORPTION AND RETENTION INDICES

The effect of this adsorption has long been recognised with an equation relating gas chromatographic retention and various partition coefficients being reported in 1961 by Martin[152]. The equation was subsequently extended by Berezkin[149] and Martire[153] and gives the net retention volume as the sum of four terms concerning (a) dissolution of the solute in the bulk of the liquid film (b) adsorption at the surface of the liquid (c) adsorption at the liquid–solid interface (d) adsorption of the solute at the non-wetted surface of the support. Adsorption has been described in appropriate texts[154] and reviews[153], and the effects only are included in this work.

Non-polar solutes and strongly polar solvents exhibit strong adsorption as they are of limited compatibility. An excess surface concentration of solute occurs as it is largely excluded from the bulk of the stationary phase. The effect also may occur with the opposite situation as observed by Martin and Gump[155] as demonstrated by squalane and polar solutes.

The Gibbs surface adsorption is a complication in retention measurement and while it may not be eliminated it may be minimised by the use of small solute samples as it is concentration dependent[154].

9. RETENTION INDEX DETERMINATION WITH COMPUTERS AND COUPLED INSTRUMENTS

The universal availability of mini-computers and microprocessors and of coupled and multi-detector instruments have continued to be reported as means of on-line and off-line determination of retention indices and or compound identification. Such methods as have been reported in recent years are usually not novel and accordingly are only briefly indicated in this work.

The automatic calculation of retention indices using both on-line and off-line operation with computing devices from simple calculators have been described by various workers[156–160], but are readily available as turn-key systems from the major instrument suppliers. Several systems of a process or pilot plant nature for the measurement and estimation of the hydrocarbons from the gasification of coal have been described[89,90]. The automatic gas chromatographic evaluation of the performance of membranes has been reported[161].

Multi-channel and multi-detector systems have also been reported[162–165] although such systems have been available for decades. Computerized gas chromatography[166] and gas chromatography–mass spectrometry[167,168] instruments have been described as have searching techniques of retention indices and mass spectra[169–171]. A retention index library of capillary chromatographic data has been developed by Sadtler Laboratories[172] and its use reported in micropollution analysis[173,174].

10. RELATIONSHIP BETWEEN RETENTION INDEX AND PHYSICO-CHEMICAL PARAMETERS

Throughout the history of chromatography there has been continued interest in relating retention parameters, including retention index, with physico-chemical quantities. The difficulty with all of these relationships is that they are restricted to

TABLE I

RECENT STUDIES ON RETENTION INDICES AND PHYSICO-CHEMICAL QUANTITIES

Property	*Ref.*
Boiling point	179–183
Density	184
Molar mass	185
Vapour pressure	185
Molar volume	186–188
Refractive index	182, 185, 187, 189
Molar refraction	181, 186–191
Thermodynamic parameters	192–195
Van der Waals volumes	182, 187, 196, 197
Dipole moment	180, 188
Capacity factors	198
Cohesion parameters	199
Electric interactions	200–202
Molecular orbitals	203
Taft and Palm constants	204
Molecular polarizability	205
Solubility factors	206
Connectivity index	182, 191, 196, 204, 207–211

a single or similar functional class with the data generally being obtained on non-polar stationary phases where the operative interactions forces are large dispersion, On polar stationary phases many of the simpler relationships are found to be non-linear.

Many workers have studied generally the various physico-chemical quantities on small groups of compounds[175–178]. Many of the widely discussed parameters —boiling point, density, refractive index, molar refraction, dipole moment, vapour pressure— have continued to attract attention while the area of most development concerns the relationship of retention indices and connectivity indices. Representatives of the reports that have appeared are shown in Table 1 with the parameters of interest being indicated.

An extremely important and simple relationship was developed by Kováts and Weisz[212], but has found little use. The retention index was shown to be related to the standard chemical potential of the solute between the ideal gas state and the ideal dilute solution if there is no adsorption at the gas–liquid interface. The relationship is shown below as eqn. 30.

$$I = 100\,\frac{\Delta\mu_s - \Delta\mu_z}{\Delta\mu_{Z+1} - \Delta\mu_Z} + 100Z \qquad (30)$$

where $\Delta\mu$ is the standard chemical potential difference between the gas phase and the solution.

An extension of the method of Laffort and Patte[213] for the calculation of solubility factors in gas chromatography has recently been refined[206] and applied to 240 compounds covering a wide range of functional classes and structures. The retention index is related by the expression shown in eqn. 31.

$$I = \alpha A + \omega O + \varepsilon E + \pi P + \beta B + 100 \qquad (31)$$

where the solubility factors are shown by the greek letters and the stationary phases by the arabic letters. The determination of liquid–liquid partition data has been reported using the 45 equations derived by Valkó and Lopata[214].

A chromatographic polarity parameter ($I - bMR$) has been reported by Kaliszan and Hoeltje[190] where MR is the molar refractivity of the solute examined and b is the stationary phase polarizability coefficient.

The coefficient b was determined by the examination of retention of two stationary phases of different polar character.

Zhang and Shi[215] have evaluated the MOSCED (modified separation of cohesive energy distances) and UNIFAC, method of Fredenslund *et al.*[216] for the prediction of retention indices by a consideration of activity coefficients at infinite dilution for a variety of organic compounds. On non-polar stationary phases with aliphatic and aromatic hydrocarbons the MOSCED predictions were found to be reasonably accurate and markedly better than those given by the UNIFAC procedure.

Relationships between both gas and liquid chromatographic retention parameters and the molecular surface area of polyhalogenated biphenyls has been reported by Hoefler *et al.*[217]. Generally the substitution of hydrogen by halogen atoms (chlorine, bromine, iodine) increased both the retention index and the calculated surface area. On the other hand, fluorine substitution led to a slight increase in molecular surface area, but a reduction in retention.

11. TABULATION OF RECENTLY REPORTED RETENTION INDEX DATA

Many or most reports concerning the retention index relate to small numbers of compounds often for some analytical purpose. These are not included in Table 2 which largely shows compilations of data of larger numbers of compounds.

12. CONCLUSIONS

The retention index has continued to find ever increasing acceptance, despite its shortcomings, particularly with polar stationary phases and where the samples and standards are of widely differing chemical classes. The problems have been known for decades but no more satisfactory general series has been introduced or is probably likely to be introduced. With the widespread use of data processing equipment the interrelation of retention systems and calibration standards is common place and leads to minimisation of some of the difficulties.

The general statement is certainly very useful that the reproducibility of retention indices based on *n*-alkane is good to excellent if the surface tension of the stationary phase is low. This is a characteristic of many non-polar stationary phases, such as hydrocarbons, methyl polysiloxanes, and in such cases retention is only due to absorption. Polar phases often behave very differently. Adsorption at the surface of the moderately polar phase, *i.e.*, polyethylene glycol[362] has been studied and it has been shown that retention data are reproducible if the specific surface area of the liquid phase is the same.

The first 25 years of the retention index scheme was exhaustively reviewed[11] to include most mentions of the retention index, and provided some 1500 reports from the literature equivalent to sixty per annum. The increasing usage of the scheme is

TABLE 2

RECENTLY REPORTED RETENTION INDEX DATA

Compounds		*Ref.*	*Note*[a]
Alkanes	C_4–C_{10}	218	a
	C_3–C_{13}, *n*-	183	a
	C_6–C_{14}, iso-	219	f
	67 C_8–C_{14}	220	a
	31 miscellaneous	221	
	63 C_6–C_9, branched	222	a
	C_3–C_7 alkylcyclopentanes	223	
	C_2–C_6 alkylcyclohexanes	223	
	Cycloheptanes	189	a
	C_{17}–C_{24}, miscellaneous	224	
	20 cyclo-	221	
	Alkenyl cyclo-	363	
	Chlorinated cyclo-	225	
	Bicyclo[4.4.0]decane stereoisomers	226, 227	
Alkenes	71 C_3–C_{13}, *n*-	220, 228	
	47 C_5–C_8	198, 229, 230	
	Cyclo	231	c
	Mono and cyclo-	232	
	Substituted cyclo-	233	
	Alkyl dicyclopentadienes	234	
	C_3–C_7 alkylcyclopentanes	223	
Alkynes	Cyclo	231	c
	Miscellaneous	198	
Hydrocarbons	C_5 petroleum	235, 236	g
	C_6	188	a
	51 hydrocarbons	97	g
	33 hydrocarbons	237	
	100 hydrocarbons	238	g
	200 hydrocarbons	239	
	Coal hydrogenate	240	d, f
	C_4–C_{10}, miscellaneous	241	
	105 C_9–C_{16}, b.p. 150–175°C	242	
	Nitrated polynuclear	243	e
	200 petroleum	244	
	43, b.p. 50–70°C	245	
	200, b.p. 0–200°C	246	
	Chlorinated C_1–C_3	247	
	26 diterpenic	248	
Aromatic	Methylbenzenes	249	
	34 alkyl	250	a
	Various alkyl	251, 252	a
	30 alkyl	253	
	Miscellaneous alkyl	186	a
	C_2–C_6 alkyl	254	
	13 alkenyl	255	a
	Monosubstituted alkyl	256	
	C_6–C_{10} monocyclic	257	
	10 polycyclic	205, 258	
	45 polycyclic	208	a

TABLE 2 (*continued*)

Compounds		*Ref.*	*Note*[a]
	polyaromatic	259, 260	
	C_{14}–C_{17}, alkyl	261	
	C_6–C_{12}, alkyl	262	f
	57 C_6–C_{14}, monocyclic	263	f
	25 C_6–C_{14}, bicyclic	263	f
	Mononitrated poly	209	
	56 nitrated	264, 265	
	Poly S- and N-heterocyclic	77	k
	Hydroxy	266	
	Methoxy	266	
	Chlorinated	266	
	Chlorinated	267	c
	Chlorinated	180	a
	51 complex	268	
	Benzene and chloro- and nitro derivatives	269	d
	Chloranisoles	270	d
	19 chloranisoles	271	
	o-Methoxyanisoles	270	d
	Isomeric chlorophenols	272	c
	Halogenated benzenes and anisoles	273	
	9 chlorinated 4-hydroxybenzaldehydes	274	
	9 chlorinated veratroles	275	
	2,5-Dichloroterephthalic acid derivatives	193	a
	Pyridines, alkyl	276	
	Pyridines, methyl	277	
	28 alkyl quinolines	278	a
	25 alkyl quinolines	279	
	24 alkyl quinoline bases	280	
	Monosubstituted pyrazines	281	a
	100 pyrazines	282	
	Alkyl diphenyls	283	c
	27 chlorinated biphenyls	284	
	57 halogenated biphenyl	217	
	7 *p*-quinones	285	
	Alkyl naphthalenes	286	
	12 Monomethylbenz[a]anthracenes	201	c
	Chlorinated dibenzo-*p*-dioxins	287	a
	9-substituted carbazoles	211	a
Drugs	Miscellaneous	288	
	275 drugs	289	
	61 drugs	290	
	101 urinary organic acids	291	
	8 basic and neutral	292	h
	Neuroleptic	293	
	175 basic	294	
	Acidic, neutral and basic	295, 296	
	16 antirheumatic	297	
	100 poisonous compounds	298	
	61 volatile compounds in blood	290	
	33 benzodiazepine drugs	299	

(*Continued on p. 118*)

TABLE 2 (*continued*)

Compounds		*Ref.*	*Note*[a]
Esters	C_1–C_{16} *n*-alkyl C_3–C_5 isoalkyl chloroacetates	300	
	C_1–C_{18} *n*-alkyl butanoates and chlorinated derivatives	301	c
	C_1–C_{18} alkyl and 2-chloro and 3-chloropropanoates	302	c
	2-, 2,2-, 2,2,2-chloroesters of C_2–C_{20} n-alkanoates	303	c
	C_1–C_{12} *n*-alkyl benzoates and pentafluorobenzoates	304	c
	C_1–C_{18} alkyl 2- and 3-chloroacetates	303	c
	C_1–C_{18} *n*-alkyl chloro, dichloro, trichloracetates	305	c
	Chlorinated methyl propanoates and butanoates	306	
	Benzoyl and monochlorobenzyl esters of unsaturated acids	307, 308	
	Unsaturated benzoic and monochlorinated esters	309	
	Benzoyl and pentafluorobenzyl esters	310	
	Ethyl and chloroethyl monochlorobenzoates	311	c
	C_1–C_{12} *n*-alkyl benzoates, 4-nitro and 3,5-dinitro derivatives	312	
	Acyl and halogenated acyl esters of unsaturated alcohols	313	
	Branched C_3–C_5 alkyl halogenated acetates	314	
	C_1–C_{10} alkyl, C_2–C_{10} alkanoates and haloalkyl derivatives	315	
	35 aliphatic esters	250	
	173 aliphatic saturated and unsaturated esters	316	
	Methyl esters of aryl aliphatic acids	317	
	C_1–C_6 *n*-, C_3–C_6 isoalkyl acrylates	318	
	C_1–C_{18} alkyl acrylates and methacrylates	319	
	Polyoxyethylene glycol diacetates	320	j
	Chloropropyl esters of aliphatic acids	321	
	Haloalkylsalicylic esters	322	
	Chlorinated phenyl acetates	323	
	9 methyl esters of resin acids	324	
	Orthophosphate esters	325	
	Barbiturate esters	326	
	Glycidic esters	327	
Miscellaneous	600 pesticides	328	b
	22 chemical warfare agents	329	h
	37 sulphur vesicants	330	h
	12 nitrogenous siloxanes	185	a
	Alkylalkoxysilanes	331	
	Silazanes and siloxazines	332	
	Trimethylsilyl amino acids	333	
	Epoxides C_4–C_5	334	
	Racemic and enantiomeric amino acids	335	f
	10 thiols	336	
	Alkyl disulphides	337	
	18 dialkyl sulphides	336	
	C_1–C_2 alkylated benzothiophenes	338	
	Substituted dibenzo[*b*,*f*]thiepins	339	c
	Constituents 14 essential oils	340	
	56 essential oil constituents	341	
	50 organic micropollutants	342	
	4 organotin compounds	343	
	Organophosphorus compounds	344	
	16 C_6 alkanols	345	
	Saturated alcohols	178	a
	Polycyclic alcohols	346	a
	2-Nitro-1-alkanols	347	

TABLE 2 (*continued*)

Compounds	*Ref.*	*Note*[a]
o-Methyl inositols	348	
Oxygenated compounds	349	
Alkyl ketones	350	h
Polyoxyethylene derivatives	351	d
Polyoxyethylene surfactants	352	j
28 heterocyclic nitrogen compounds	210	a
68 monoalkylnitrogen heterocyclic compounds	210	a
15 oxygen-containing adamantanes	353	f
Secondary aliphatic amines	354	a
Secondary amines	355	a
Aliphatic and heterocyclic amines	356	
Formamidines, N,N'-dialkyl	357	
Formamidines, N,N'-dimethyl	358	
207 dimethylbenzamidines and benzylidene amines	359	
Alkyl porphyrins	360	
7 triochothecenes	361	

[a] Notes: a = correlations with physico-chemical properties; b = emergence temperatures; c = I + retention increments; d = retention increments; e = I and PAH indices; f = I and temperature dependence; g = unified retention indices; h = programmed indices; i = electronic interaction indices; j = arithmetic retention indices; k = Lee indices.

indicated in this —a very selective— review where the majority of works containing data of a few compounds have been omitted; nevertheless the bibliography is proportionately much greater.

13. ACKNOWLEDGEMENTS

The authors wish to express their appreciation of the painstaking assistance of Miss Jane Fordham and to Professor Kováts for his comments on this manuscript.

14. SUMMARY

The development of the retention index over 30 years is summarised and advances that have occurred in recent years are highlighted.

The work follows an exhaustive review published by Budahegyi *et al.* in 1983, but is much more selective and does not include the many reports of isolated retention indices.

The review includes alternative logarithmic index schemes and other reference series that have been reported and which were not included in the earlier work. The work concludes with a tabulation of recently available compilations of retention indices.

15. NOTE ADDED IN PROOF

This article is based upon a paper presented at the *17th International Symposium on Chromatography* held in Vienna, 25–30 September 1988. From the onset it was the authors' intention to present a selective account of recent developments in Kovats' retention index and related retention scales. In this respect it may be regarded as being complementary to the accompanying article by Dr. Takács and his co-workers (this issue, pp. 1–92). Together we believe that the combined articles will represent the most comprehensive and authoritative account of Kovats' retention index scheme to have been published to date.

REFERENCES

1 E.sz. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
2 F. P. Woodford and C. M. van Gent, *J. Lipid Res.*, 1 (1960) 188.
3 T. K. Miwa, K. J. Mikoljczak, F. P. Earle and I. A. Wolft, *Anal. Chem.*, 32 (1960) 1739.
4 F. J. Vandenheuvel and E. C. Horning, *Biochim. Biophys. Acta*, 64 (1962) 416.
5 E. C. Horning, F. J. Vandenheuvel and B. G. Greech, in D. Glick (Editor), *Methods of Biochemical Analyses*, Vol. XI, Interscience, New York, 1963, pp. 69–147.
6 *Second International Symposium on Gas Chromatography, Houston, IX, 1964*, abstracts.
7 L. S. Ettre, *Anal. Chem.*, 36 (1964) 31A.
8 E.sz. Kováts, *Adv. Chromatogr.*, 1 (1965) 229.
9 J. K. Haken, *Adv. Chromatogr.*, 14 (1976) 367.
10 L. S. Blomberg, *Adv. Chromatogr.*, 27 (1987) 226.
11 M. V. Budahegyi, E. R. Lombosi, T. S. Lombosi, S. Y. Mészáros, Sz. Nyiredy, G. Tarján, I. Timár and J. M. Takács, *J. Chromatogr.*, 271 (1983) 213.
12 L. Szepesy, K. Lasing and L. Podmaniczky, *Magy. Kem. Lapja*, 40 (1985) 103.
13 T. Tóth, *Magy. Kem. Lapja*, 40 (1985) 114.
14 X. Luo, X. Wong and L. Cheng, *Gaodeng Kuexiao Huaxue Xuebao*, 5 (1985) 61.
15 M. Singliar, *Petrochemia*, 26 (1986) 141.
16 C. Dia, P. Lu and H. Li, *Sepu.*, 6 (1988) 81.
17 M. Singliar, *Petrochemia.*, 27 (1987) 4.
18 H. van den Dool and P. D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
19 E. R. Adlard, A. G. Butlin, M. B. Evans, R. S. Evans, R. Hill, J. F. K. Huber, A. B. Littlewood, W. H. McCambley, J. F. Smith, W. T. Swanton and P. A. T. Swoboda, in A. Goldup (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1965, p. 313.
20 M. B. Evans, *Chromatographia*, 6 (1973) 301.
21 E. sz. Kováts, *Z. Anal. Chem.*, 181 (1961) 351.
22 A. Wehrli and E. sz. Kováts, *Helv. Chim. Acta*, 42 (1959) 2709.
23 J. Zulaica and G. Guiochon, *C.R. Hebd. Seances. Acad. Sci.*, 225 (1962) 524.
24 J. Zulaica and G. Guiochon, *Bull. Soc. Chem. France*, (1963) 1242.
25 J. K. Haken, *J. Chromatogr.*, 99 (1974) 329.
26 A. Matukuma, in C. L. A. Harbourn and R. Stock (Editors), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 55.
27 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 5 (1961) 300.
28 P. A. T. Swoboda, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworth, London, DC, 1962, p. 273.
29 M. Huguet, in J. Tranchant (Editor), *Journées International d'Études de Méthodes de Séparation Immediate et de Chromatographie*, GAMS, Paris, 1961.
30 J. F. Smith, *Chem. Ind. (London)*, (1960) 1024.
31 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 6 (1961) 293.
32 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 9 (1962) 147.
33 F. J. Vandenheuvel, W. C. Gardner and E. C. Horning, *Anal. Chem.*, 36 (1964) 1550.
34 M. R. Guerin and C. V. Banks, *J. Gas Chromatogr.*, 4 (1966) 428.

35 J. R. Ashes, J. K. Haken, S. C. Mills, *J. Chromatogr.*, 187 (1980) 297.
36 L. J. Lorenz and L. B. Rogers, *Anal. Chem.*, 43 (1971) 1593.
37 H. F. Dymond and K. D. Kilburn, in A. B. Littlewood (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 353.
38 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 535.
39 A. Grobler, *J. Chromatogr. Sci.*, 10 (1972) 128.
40 S. J. Hawkes, *J. Chromatogr. Sci.*, 10 (1972) 536.
41 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103.
42 U. Heldt and H. J. K. Köser, *J. Chromatogr.*, 192 (1980) 107.
43 J. Novák and J. Růžičková, *J. Chromatogr.*, 91 (1974) 79.
44 G. Castello and G. D'Amato, *J. Chromatogr.*, 131 (1977) 41.
45 J. Raymer, D. Wiesler and M. Novotny, *J. Chromatogr.*, 325 (1985) 13.
46 L. Mathiasson, J. Å. Jonsson, A. M. Olson and L. Haraldson, *J. Chromatogr.*, 152 (1978) 11.
47 M. S. Wainwright, C. S. Nieass, J. K. Haken and R. P. Chaplin, *J. Chromatogr.*, 321 (1985) 287.
48 A. B. Littlewood, *J. Gas Chromatogr.*, 1 (1963) 16.
49 W. A. Aue and V. Paramasigamani, *J. Chromatogr.*, 166 (1978) 253.
50 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 41 (1969) 313.
51 M. Boguz, J. Wysbeck, J. P. Franke and R. A. de Zeeuw, *J. Anal. Toxicol.*, 7 (1983) 188.
52 B. Kolb, M. Auer and P. Popisol, *J. Chromatogr. Sci.*, 15 (1977) 53.
53 A. Eklund, J. Jonsson and J. Schuberth, *J. Anal. Toxicol.*, 7 (1983) 24.
54 R. A. de Zeeuw, M. Bogusz, J. P. Franke and J. Wijsbeek, in R. C. Basett (Editor), *Advances in Analytical Toxicology*, Vol 1. Biomedical Publications, Foster City, CA, 1984, p. 41.
55 W. M. Asselin, *J. Chromatogr. Sci.*, 24 (1986) 444 55A.
56 L. N. Zotov, G. V. Golovkin and R. V. Golovnya, *J. High. Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 6.
57 J. Enqvist, P. Sunila and U.-M. Lakkisto, *J. Chromatogr.*, 279 (1983) 667.
58 M. B. Evans, *J. Chromatogr.*, 12 (1963) 2.
59 H. Neu, M. Zell and K. Ballschmitter, *Fresenius' Z. Anal. Chem.*, 293 (1978) 192.
60 K. Ballschmitter and H. Neu, *Fresenius' Z. Anal. Chem.*, 302 (1980) 20.
61 K. Ballschmitter and Ch. Unglert and H. Neu, *Chemosphere*, 6 (1977) 51.
62 T. R. Schwartz, J. D. Petty and E. M. Kaiser, *Anal. Chem.*, 55 (1983) 1839.
63 T. R. Schwartz, R. D. Campbell, D. L. Stalling, R. L. Little, J. D. Petty, J. W. Hogan and E. M. Kaiser, *Anal. Chem.*, 56 (1984) 1308.
64 R. C. C. Wegman and A. W. H. Hofstee, *Report EUR 10388*, *Organic Micropollutants in Aquatic Environments 162-6*, Commission of the European Communities, Brussels, 1986.
65 F. J. Heeg and R. Zinburg, *Intell. Instr. Comput.*, 4 (1986) 249.
66 A. Yasuhara, M. Morita and K. Fuwa, *J. Chromatogr.*, 328 (1985) 35.
67 S. J. Fernandez, L. P. Murphy, F. A. Hohorst and R. A. Rankin, *Anal. Chem.*, 56 (1984) 1285.
68 F. Pacholec and C. F. Poole, *Anal. Chem.*, 54 (1982) 1019.
69 F. Pacholec, *Ph.D. Thesis*, Wayne State University, Detroit, MI, 1983.
70 F. Pacholec and C. F. Poole, *J. Chromatogr.*, 302 (1987) 289.
71 G. L. Hall, W. E. Whitehead, C. R. Mourer and T. Shibamoto, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 266.
72 V. W. Watts, T. F. Simonick, *J. Anal. Toxicol.*, 11 (1987) 210.
73 A. Nakamura, R. Tanaka and T. Kashimoto, *J. Assoc. Off. Anal. Chem.*, 67 (1984) 129.
74 A. Nakamura, *Shokakin Eisee Hun.*, 16 (1983) 69.
75 R. P. Kozlosku, *J. Chromatogr.*, 318 (1985) 211.
76 M. L. Lee, D. L. Vassilaros and C. M. White, *Anal. Chem.*, 51 (1979) 768.
77 D. L. Vassilaros, R. C. Kong, D. W. Later and M. L. Lee, *J. Chromatogr.*, 252 (1982) 1.
78 M. L. Yu and R. Hites, *Anal. Chem.*, 53 (1981) 951.
79 J. A. Yergey, T. H. Risby and S. S. Lestz, *Anal. Chem.*, 54 (1982) 354.
80 G. Alexander and I. Hazai, *J. Chromatogr.*, 217 (1981) 19.
81 C. Willey, M. Iwao, R. N. Castle and M. L. Lee, *Anal. Chem.*, 53 (1981) 40.
82 D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong and D. L. Vassilaros, *Anal. Chem.*, 53 (1981) 1612.
83 D. L. Vassilaros, P. W. Stoker, G. M. Booth and M. L. Lee, *Anal. Chem.*, 54 (1982) 106.
84 D. L. Vassilaros, D. A. Eastmond, W. R. West, M. L. Lee and G. M. Boot, in *Proc. 6th Int. Symp. on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 27–29, 1981*, Battelle Press, Columbus, OH, 1982.

85 D. V. Grass, J. W. de Leeuw, P. A. Schenk and J. Haverkamp, *Geochim. Cosmochim. Acta*, 45 (1981) 2465.
86 M. L. Lee, D. L. Vassilaros and D. W. Later, *Inst. J. Environ. Anal. Chem.*, 11 (1982) 251.
87 S. Krishnan and R. A. Hites, *Anal. Chem.*, 53 (1981) 342.
88 C. E. Rostad and W. E. Pereira, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 328.
89 P. A. Hesbach, S. C. Lamey and W. C. Green, *GC assay of Polynuclear Aromatic Hydrocarbons, Report DOE/METC-86-46901*, Morgantown Energy Technology Centre, Morgantown, WV, 1986, 24 pp.
90 V. C. Stamoudis and J. C. Demirgian, *Report DOE/MC/49682-1836, ANL/SER-5*, Argonne National Laboratory, Argonne, IL, 1985, 55 pp.
91 R. P. Kozlosku, *J. Chromatogr.*, 318 (1985) 211.
92 D. E. Wells, M. J. Gillespie and A. E. A. Porter, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 443.
93 A. Manninen, M.-L. Kuitunen and L. Julin, *J. Chromatogr.*, 394 (1987) 465.
94 Anonymous, *Air Monitoring as a Means of Chemical Disarmament*, Ministry for Foreign Affairs of Finland, Helsinki, 1985.
95 I. G. Zenkevich, *J. Anal. Chem. USSR (Engl. Transl.)*, 39 (1984) 1038.
96 N. Dimov, *J. Chromatogr.*, 347 (1985) 366.
97 S. Boneva and N. Dimov, *Chromatographia*, 21 (1986) 697.
98 D. Papazova and N. Dimov, *J. Chromatogr.*, 356 (1986) 320.
99 E. Stoyanov and N. Dimov, *Anal. Chim. Acta*, 201 (1987) 207.
100 D. Papazova and N. Dimov, *Chromatographia*, 25 (1988) 177.
101 P. G. Robinson and A. L. Odell, *J. Chromatogr.*, 75 (1971) 1.
102 N. P. Dimov, *J. Chromatogr.*, 360 (1986) 25.
103 V. G. Berezkin, *J. Chromatogr.*, 91 (1974) 559.
104 J. Riks, K. Leuten, C. Cramers and V. G. Berezkin, *Zh. Anal. Khim.*, 29 (1974) 858.
105 V. G. Berezkin and V. N. Retunsky, *J. Chromatogr.*, 292 (1984) 9.
106 J. Krupcik, E. Matisova, J. Garay, L. Sojak and V. G. Berezkin, *Chromatographia*, 16 (1982) 166.
107 E. Matisova, J. Krupcik and J. Garaj, *Chromatographia*, 16 (1982) 169.
108 V. G. Berezkin, L. F. Lebedinskaya, N. S. Nikitina, N. A. Prokopenko, N. A. Fateeva, L. V. Chulpanova, I. V. Shikalova and Ya. I. Yashin, *J. Anal. Chem. USSR (Engl. Transl.)*, 38 (1983) 1125.
109 G. Gusev, S. Rang, V. G. Berezkin and A. Orav, *Eesti NSV Tead. Akad. Toim,.Keem.*, 35 (1986) 205.
110 N. F. Belyaev and M. S. Vigdergauz, *J. Anal. Chem. USSR (Engl. Transl.)*, 41 (1986) 1678.
111 N. F. Belyaev and M. Vigdergauz, *Zh. Anal. Khim*, 43 (1988) 867.
112 M. B. Evans and J. F. Smith, *Nature (London)*, 190 (1961) 905.
113 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 8 (1962) 303.
114 M. B. Evans, *Chromatographia*, 2 (1969) 397.
115 M. B. Evans, *Chromatographia*, 11 (1978) 183.
116 J. K. Haken and D. Srisukh, *J. Chromatogr.*, 199 (1988) 199.
117 O. Piringer, M. Jalobeanu and U. Stănescu, *J. Chromatogr.*, 119 (1976) 423.
118 I. G. Zenkevich and A. S. Malamakhov, *Vestn. Leningr. Univ., Fiz. Khim.*, 4, No. 2 (1987) 101.
119 M. B. Evans, J. K. Haken and T. Tóth, *J. Chromatogr.*, 351 (1986) 155.
120 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 389 (1987) 240.
120 J. K. Haken and R.-J. Smith, *J. Chromatogr.*, 452 (1988) 31.
122 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 471 (1989) 217.
123 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 462 (1989) 31.
124 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 468 (1989) 373.
125 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 406 (1987) 105.
126 J. Yamaguchi and T. Hanai, *Chromatographia*, in press.
127 T. Hanai and J. Hubert, *J. Chromatogr.*, 290 (1984) 197.
128 Y. Arai, M. Hirukawa and T. Hanai, *J. Chromatogr.*, 384 (1987) 279.
129 M. S. Vigdergauz, in H. G. Struppe (Editor), *Gas Chromatographie 1968—6th Symposium on Gas Chromatographie*, Akademie-Verlag, Berlin, 1968, p. 625.
130 M. S. Vigdergauz and A. A. Martynov, *Chromatographia*, 4 (1971) 463.
131 C. L. A. Harbourn cited by A. C. Douglas, *J. Chromatogr. Sci.*, 7 (1969) 581.
132 G. W. K. Cavill and E. Houghton, *Aust. J. Chem.*, 26 (1973) 1131.
133 G. W. K. Cavill and E. Houghton, *Aust. J. Chem.*, 27 (1974) 879.
134 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 184 (1980) 1.

135 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 334 (1985) 95.
136 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 328 (1985) 11.
137 M. S. Wainwright and J. K. Haken and D. Srishuhk, *J. Chromatogr.*, 188 (1980) 246; and references cited therein.
138 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
139 J. R. Ashes, S.-C. Mills and J. K. Haken, *J. Chromatogr.*, 166 (1978) 391.
140 R. Feinland, A. J. Andreatch and D. P. Cotrupe, *Anal. Chem.*, 33 (1961) 991.
141 J. F. Smith, *Nature (London)*, 193 (1962) 679.
142 J. F. Parcher and D. M. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 267.
143 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 256 (1983) 193.
144 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 331 (1985) 389.
145 G. Schomburg and G. Dielmann, *J. Chromatogr. Sci.*, 11 (1973) 151.
146 M. Goedert and G. Guiochon, *Anal. Chem.*, 42 (1970) 962.
147 M. Goedert and G. Guiochon, *Anal. Chem.*, 45 (1973) 158.
148 L. S. Ettre, *Chromatographia*, 6 (1973) 489.
149 V. G. Berezkin, *J. Anal. Chem. USSR (Engl. Transl.)*, 40 (1985) 459.
150 J. Krupčik, E. Matisova, J. Garaj, L. Sojak and V. G. Berezkin, *Chromatographia*, 16 (1982) 166.
151 E. Matisiva, J. Krupčik and J. Garaj, *Chromatographia*, 16 (1982) 169.
152 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
153 D. Martire, in J. H. Purnell (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1968, p. 93.
154 J. R. Conder and C. L. Young, *Physicochemical Applications of Gas Chromatography*, Wiley, Chichester, 1979.
155 R. L. Martin and B. G. Gump, *J. Phys. Chem.*, 71 (1967) 2202.
156 H. J. Huizing, in K.-H. Kubeczka (Editor), *Aetherische Oele, Erget. Int. Arbeitstag 1979–1980*, Thieme, Stuttgart, 1981, p. 123.
157 E. Ziegler, B. Weimann, I. Wronka, G. Schomburg and V. Haevsig, *Anal. Chim. Acta*, 147 (1983) 91.
158 H. Li, X. Chaozheng, F. Xu and P. Lu, in P.-C. Lu and E. Bayer (Editors), *Proc. Sino-West German Symp. Chromatography 1981*, Science Press, Beijing, 1982.
159 X. Wang, *Shenyang Yaoxueyuan, Xuebaco*, 1 (1984) 51.
160 N. F. Belyaev, M. S. Vigdergauz and M. I. Matusov, *Zavod. Lab.*, 52 (1987) 1.
161 N. G. Castello and G. Tealdo, *J. Chromatogr.*, 395 (1987) 437.
162 J. Enquist and A. H'Esso, *Kem-Kemi*, 9 (1982) 176.
163 H. Pyysalo, J. Enquist, J. Sandholm and P. Sunila, in R. Marcuse (Editor), *Proc. Scand. Symp. on Lipids, 12th Meeting 1983*, Lipid Forum, Göteborg, 1984, p. 11.
164 J. Enquist, M. Kokko, M. Pajarinen and M. Ulla, *Kem-Kemi*, 12 (1985) 793.
165 C. O'Donnell and P. M. Larkin, *Report EUR10388*, *Organic Micropollutants in Aquatic Environment*, Commission of the European Communities, Brussels, 1986, p. 128.
166 J. C. Demirgian, *J. Chromatogr. Sci.*, 22 (1984) 153.
167 K. Kemmotsu, M. Kondo, M. Izumi, K. Matsunago and T. Ishida, *Okayama-Ken, Kanko Hoken Senta Nenpo*, 8 (1984) 189.
168 P. J. Marriott, J. P. Gill, R. P. Evershed, C. S. Hein and G. Eglington, *J. Chromatogr.*, 301 (1984) 107.
169 K. Masumoto and T. Yamamoto, *Annual Report, Osaka City Inst. Public Health Environ. Sci.*, 47 (1984) 1.
170 H. Yamuda, K. Harada, S. Nakamura and S. Mihara, *J. SCCJ*, 21 (1987) 30.
171 C. Boniface, G. Vernin and J. Metzger, Analusis, 15 (1987) 564.
172 J. F. Sprouse and A. Varano, *Am. Lab.*, 16 No. 9 (1984) 54.
173 L. Wever, in P. Sandra (Editor), *Proc. 6th Int. Symp. Capillary Chromatography*, Hüthig, Heidelberg, 1986, p. 330.
174 L. Weber, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 446.
175 J. Bermejo and M. D. Guillen, *Chromatographia*, 17 (1983) 664.
176 L. Podmaniczky, L. Szepesy, K. Lakaszner and G. Schomburg, *Chromatographia*, 20 (1985) 623.
177 A. M. Afanasev, V. N. Demeshev, E. P. Kalyazin and G. V. Kovalev, *Chromatographia*, 21 (1986) 95.
178 J. Bermejo and M. D. Guillen, *Anal. Chem.*, 59 (1987) 94.
179 F. Saura-Calixto, A. Garcia-Raso, J. Cannelas and J. Garcia-Raso, *J. Chromatogr. Sci.*, 21 (1983) 267.
180 P. P. Alikhanov, K. I. Sakodynskii and G. N. Kuznetsova, *Zh. Anal. Khim.*, 42 (1987) 712.
181 J. Bermejo and M. D. Guillen, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 22.

182 V. M. Nabivach and V. E. Vasilev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 30 (1987) 72.
183 L. Wu, *Sepu.*, 4 (1986) 197.
184 N. Dimov and S. Boneva, *Izv. Khim.*, 19 (1986) 456.
185 T. I. Rybkina, E. A. Kirichenko, V. A. Kochetova and V. M. Kopylov, *Zh. Anal. Khim.*, 41 (1986) 2254.
186 J. Bermejo, G. G. Blanco, M. A. Diez and M. D. Guillen, *Chromatographia*, 23 (1987) 33.
187 J. Bermejo, J. S. Canga, O. M. Gayol and M. D. Guillen, *J. Chromatogr. Sci.*, 22 (1984) 252.
188 C. Chelghoum, Y. Haddad, K. Abdeddaim and M. H. Guermouche, *Analusis*, 14 (1986) 49.
189 B. G. Udarov, E. N. Manukov, O. G. Vyglazov, V. A. Ckuiko and L. V. Izotova, *Khim. Prir. Soedin.*, 22 (1986) 427.
190 R. Kaliszan and H. D. Hoeltje, *J. Chromatogr.*, 324 (1982) 303.
191 M. Kuchař, S. H. Tomková, V. Rejholec and O. Skalická, *J. Chromatogr.*, 333 (1985) 21.
192 A. Voelkel, *J. Chromatogr.*, 387 (1987) 95.
193 L. N. Sharifyanova and M. S. Vigdergauz, *Zh. Anal. Khim.*, 36 (1981) 2221.
194 W. Fuan, D. Jiang and X. Tang, *Fenxi Huaxue*, 12 (1984) 1070.
195 W. Fuan and Y. Ma, *Fenxi Huaxue*, 15 (1987) 838.
196 F. Calixto-Saura and A. Garcia-Raso, *Chromatographia*, 15 (1982) 521.
197 F. Calixto-Saura and A. Garcia-Raso, *Chromatographia*, 15 (1982) 771.
198 A. Orav, K. Kuningas, S. Rang and O. Eisen, *Eesti NSV Tead. Akad. Toim., Keem*, 34 (1985) 105.
199 A. Munafo, M. Buchmann, T. H. Nam, U. W. Kesselring, *J. Pharm. Soc.*, 77 (1988) 169.
200 H. Lamparczyk and A. Radecki, *Chromatographia*, 18 (1984) 615.
201 H. Lamparczyk and R. J. Ochocka, *Chromatographia*, 21 (1986) 409.
202 H. Lamparczyk, *Chromatographia*, 20 (1985) 283.
203 A. Garcia-Raso, F. Saura-Calixto and M. A. Raso, *J. Chromatogr.*, 302 (1984) 107.
204 P. Buryan, J. Macák, J. Třiska, L. Vodička, Yu. S. Berlizov, V. R. Omitrikov and V. M. Nabivach, *J. Chromatogr.*, 391 (1987) 89.
205 H. Lamparczyk, D. Wilczynska and A. Radecki, *Chromatographia*, 17 (1983) 300.
206 F. Patte, M. E. Tcheto and P. Laffort, *Anal. Chem.*, 54 (1982) 2239.
207 H. Masuda and S. Mihara, *J. Chromatogr.*, 366 (1986) 373.
208 B. A. Rudenko, Z. Bulycheva and L. V. Dylevskaya, *Z. Anal. Khim.*, 39 (1984) 344.
209 A. Robbat, N. Corso, P. Nicholas, P. J. Doherty and D. Marshall, *Anal. Chem.*, 58 (1986) 2072.
210 O. Papp, G. Szász, M. Farkas, M. Simon and I. Hermecz, *J. Chromatogr.*, 403 (1987) 19.
211 W. Chen, X. Chen and Y. Wang, *Fenxi Huaxue*, 12 (1984) 688.
212 E. sz. Kováts and P. B. Weisz, *Ber. Bunsenges. Phys. Chem.*, 69 (1965) 812.
213 P. Laffort and F. Patte, *J. Chromatogr.*, 126 (1976) 625.
214 K. Valkó and A. Lopata, *J. Chromatogr.*, 252 (1982) 77.
215 J. Zhang and M. Shi, *Sepu.*, 6 (1988) 133.
216 A. Fredenslund, M. L. Michelsen and P. Rasmussen, *Proc. Chem. Comp.*, 4 (1982) 35.
217 F. Hoefler, M. Melzer, J. Herman, L. W. Robertson and E. Anklam, *J. Agric. Food Chem.*, 36 (1988) 961.
218 F. Wang and G. Wang, *Shiyou Huagong*, 16 (1987) 439.
219 V. A. Terentev, *Zh. Anal. Khim.*, 42 (1987) 1870.
220 S. Rang, K. Kuningas, T. Strenze, A. Orav and O. Eisen, *J. Chromatogr.*, 406 (1987) 75.
221 S. Boneva, *God. Vissh. Khim.-Tekhnol. Inst. Burgas Bulg.*, 20 (1985) 69.
222 L. Wu, *Sepu.*, 1 (1984) 122.
223 A. Orav, K. Kuningas, S. Rang and O. Eisen, *Eesti NSV Tead. Akad. Toim., Keem.*, 31 (1982) 40.
224 J. Kuśmierz, E. Maliński, W. Czerwiec and J. Szafranek, *J. Chromatogr.*, 331 (1985) 219.
225 J. K. Haken and F. Vernon, *J. Chromatogr.*, 361 (1986) 57.
226 S. Rang, E. Kh. Kurashova, I. A. Musaev, T. V. Strenze, E. Joepera, O. Eisen and P. I. Sanin, *Neftekhimiya*, 22 (1982) 303.
227 A. J. Lubeck and D. L. Sutton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 542.
228 S. Boneva, *Izv. Khim.*, 19 (1986) 460.
229 N. Dimov and S. Boneva, *Izv. Khim.*, 19 (1986) 456.
230 S. Boneva and N. Dimov, *Chromatographia*, 21 (1986) 149.
231 W. Engewald, U. Billing, T. Welsch and G. Haufe, *Chromatographia*, 23 (1987) 590.
232 J. Bermejo, C. G. Blanco, M. A. Diez and M. D. Guillen, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 461.
233 O. Buchman, G.-Y. Cao and C. T. Peng, *J. Chromatogr.*, 312 (1984) 75.

234 J. Bermejo, C. G. Blanco, M. A. Diez and J. Suarez, *Canga Afinidad*, 40 (1983) 320.
235 A. J. Lubeck and D. L. Sutton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 328.
236 D. Papazova, R. Milina and N. Dimov, *Chromatographia*, 25 (1988) 177.
237 C. F. Chien, M. M. Kopecni and R. J. Lamb, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 539.
238 J. Krupčik, D. Repka, T. Hevesi and G. Anders, *J. Chromatogr.*, 407 (1987) 65.
239 P. C. Hayes and E. W. Pitzer, *Kovats Indices in the Characterization of Hydrocarbon Fuels, Report A F WAL-TR-81-2102*, Wright-Patterson Air Force Base, OH, 1981, 85 pp.
240 T. K. Goswami, D. K. Mukherjee, G. D. Mitra and C. N. Das, *Fuel Sci. Technol.*, 3 (1984) 117.
241 J. Wu and W. Lu, *Sepu.*, 1 (1984) 11.
242 S. S. Berman, I. M. Sokolova, I. A. Matveeva and A. A. Petrov, *Neftekhimiya*, 24 (1984) 748.
243 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 322 (1985) 71.
244 P. C. Hayes, Jr. and E. W. Pitzer, *J. Chromatogr.*, 253 (1982) 179.
245 N. G. Johansen and L. S. Ettre, *Chromatographia*, 15 (1982) 625.
246 W. G. Sovocool and N. K. Wilson, *J. Org. Chem.*, 47 (1982) 4032.
247 P. Kusz, A. Andrysiak, W. Czelakowski and J. Bobiński, *J. Chromatogr.*, 254 (1983) 163.
249 N. B. Perry and R. T. Weavers, *J. Chromatogr.*, 284 (1984) 478.
249 R. V. Golovnya, A. L. Samusenko and V. A. Lyapin, *Zh. Anal. Khim.*, 43 (1988) 311.
250 J. Bermejo and M. D. Guillen, *J. Chromatogr.*, 318 (1985) 187.
251 J. Bermejo and M. D. Guillen, *Chromatographia*, 17 (1983) 664.
252 J. Macák, V. M. Nabivach, P. Buryan and S. Šindler, *J. Chromatogr.*, 234 (1982) 285.
253 F. Wang, *Sepu.*, 4 (1986) 258.
254 E. Engewald, I. Topalova, N. Petsev and Kh. Dimitrov, *Chromatographia*, 23 (1987) 561.
255 I. Topalovia, Kh. Chanev, N. Petsev and Kh. Dimitrov, *Izv. Khim.*, 19 (1986) 444.
256 F. Vernon and J. B. Suratman, *Chromatographia*, 17 (1983) 600.
257 E. E. Kugucheva and V. I. Mashinskii, *Zh. Anal. Khim.*, 38 (1983) 2023.
258 C. N. Ho, J. R. Kennedy, G. R. Samyajula, D. Karlesky and I. M. Warner, *Report DOE/ER/60100-5*, 1984, 13 pp.; *Energy Res. Abstr.*, 9 (23) (1984) 48 250.
259 G. I. Gulko and M. I. Aliev, *Neftekhim. Protessov Mamedalieva Akad. Nauk. AZ SSR*, 12 (1982) 125.
260 B. A. Rudenko, Z. Yu. Bulycheva, V. N. Topunov and L. B. Itsikaon, *Zh. Anal. Khim.*, 39 (1984) 700.
261 L. Sojak, I. Ostrovsky, P. Farkas and P. Skalak, *Ropa. Uhlie*, 25 (1983) 149.
262 V. A. Gerasimenko and V. M. Nabivach, *Zh. Anal. Khim.*, 37 (1982) 110.
263 V. A. Gerasimenko and V. M. Nabivach, *Zh. Anal. Khim.*, 43 (1988) 109.
264 R. H. Rohrbauch and P. C. Jurs, *Anal. Chem.*, 58 (1986) 1210.
265 C. M. White, A. Robbat and R. M. Hoes, *Chromatographia*, 17 (1983) 605.
266 I. O. O. Korhonen, *J. Chromatogr.*, 321 (1985) 115.
267 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 265 (1983) 323.
268 T. Kodama, F. Morishita and T. Kojima, *Bunseki Kagaku*, 34 (1985) 282.
269 I. O. O. Korhonen, *J. Chromatogr.*, 363 (1986) 277.
270 I. O. O. Korhonen, *J. Chromatogr.*, 321 (1985) 467.
271 I. O. O. Korhonen, *J. Chromatogr.*, 294 (1984) 99.
272 I. O. O. Korhonen, *J. Chromatogr.*, 315 (1984) 185.
273 J. K. Haken and V. F. Vernon, *J. Chromatogr.*, 361 (1986) 57.
274 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, 292 (1984) 345.
275 I. O. O. Korhonen, J. Knuutinen and R. Jääskeläinen, *J. Chromatogr.*, 287 (1984) 293.
276 M. Novrocikova, J. Novrocik and J. Vymetal, *Collect. Czech. Chem. Commun.*, 48 (1983) 3270.
277 R. V. Golovnya, A. L. Samusenko and L. B. Dmitriev, *Zh. Anal. Khi,.*, 42 (1987) 699.
278 P. Buryan, J. Macak, J. S. Berlizova and V. M. Nabivach, *Chem. Prum.*, 36 (1986) 88.
279 Yu. S. Berlizov, V. M. Nabivach and V. P. Dimitiev, *Zh. Anal. Khim.*, 42 (1987) 1119.
280 Yu. S. Berlizov, V. M. Nabivach, P. Buryana and J. Macak, *Sb. Vys. Sk. Chem-Technol. Praze, Technol. Paliv*, D51 (1985) 147.
281 H. Masuda and S. Mihara, *J. Chromatogr.*, 366 (1986) 373.
282 S. Mihara and N. Enomoto, *J. Chromatogr.*, 324 (1985) 428.
283 J. Novrocik, M. Novrocikova and J. Foniok, *Collect, Czech. Chem. Commun.*, 491 (1984) 218.
284 W. T. Foreman and T. F. Bidleman, *J. Chromatogr.*, 330 (1985) 203.
285 A. Llobera and A. Garcia-Raso, *J. Chromatogr.*, 393 (1987) 305.
286 A. M. Afanasev, V. N. Demeshev, E. P. Kalyazin and G. V. Kovalev, *Chromatographia*, 21 (1986) 95.

287 J. R. Donnelly, W. D. Munslow, R. K. Mitchum and G. W. Sovocool, *J. Chromatogr.*, 392 (1987) 51.
288 B. Newton and R. T. Foery, *J. Anal. Toxicol.*, 8 (1984) 129.
289 E. Marozzi, V. Gambaro, E. Saligari, R. Mariani and F. Lodi, *J. Anal. Toxicol.*, 6 (1982) 185.
290 R. Uehori, T. Nagata, K. Kimura, K. Kudo and M. Noda, *J. Chromatogr.*, 411 (1987) 251.
291 M. Tuchman, L. D. Bowers, K. D. Fregien, P. J. Crippen and W. Krivit, *J. Chromatogr. Sci.*, 22 (1984) 198.
292 M. Bogusz, J. Wijsbeek, J. P. Franke, R. A. de Zeeuw and J. Gierz, *J. Anal. Toxicol.*, 9 (1985) 49.
293 L. Buydens, D. L. Massart and P. Geerlings, *Anal. Chim. Acta*, 174 (1985) 237.
294 W. H. Anderson and D. T. Stafford, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 247.
295 M. Bogusz, J. Wijsbeek, J. P. Franke and R. A. de Zeeuw, *J. Anal. Toxicol.*, 7 (1983) 188.
296 D. W. Christ, P. Noomano, M. Ross and D. Rhone, *J. Anal. Toxicol.*, 12 (1988) 84.
297 J. Macek and E. Smolková-Keulemansová, *J. Chromatogr.*, 233 (1985) 309.
298 N. Oyama, T. Sano, M. Syoyama and K. Maeda, *Eisei Kagaku*, 33 (1987) 342.
299 M. Japp, K. Garthwaite, A. V. Geeson and M. D. Osselton, *J. Chromatogr.*, 439 (1988) 317.
300 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 244 (1982) 142.
301 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 320 (1985) 325.
302 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 319 (1985) 131.
303 I. O. O. Korhonen, *J. Chromatogr.*, 329 (1985) 43.
304 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 328 (1985) 325.
305 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 256 (1983) 22.
306 I. O. O. Korhonen, J. Knuutinen and R. Jääskeläinen, *J. Chromatogr.*, 287 (1984) 293.
307 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 323 (1985) 331.
308 J. K. Haken, B. G. Madden and I. O. O. Korhonen*J. Chromatogr.*, 325 (1985) 61.
309 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 324 (1985) 113.
310 I. O. O. Korhonen, *J. Chromatogr.*, 329 (1985) 359.
311 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 325 (1985) 433.
312 I. O. O. Korhonen, *J. Chromatogr.*, 356 (1986) 285.
313 I. O. O. Korhonen, *J. Chromatogr.*, 288 (1984) 329.
314 I. O. O. Korhonen, *J. Chromatogr.*, 288 (1984) 51.
315 I. O. O. Korhonen, *J. Chromatogr.*, 357 (1986) 107.
316 J. R. Chrétien and K. Szymoniak, *J. Chromatogr.*, 406 (1987) 95.
317 M. Kuchař, S. H. Tomková, V. Rejholec and O. Skalická, *J. Chromatogr.*, 333 (1985) 21.
318 A. Horna, J. Táborský, J. Churáček and O. Dufka, *J. Chromatogr.*, 348 (1985) 141.
319 A. Horna, J. Táborský, O. Dufka, P. Mtoušek and J. Churáček, *J. Chromatogr.*, 325 (1985) 367.
320 J. Szymanovski, H. Szewczyk and B. Atamanczuk, *Tenside Detergents*, 19 (1982) 70.
321 K. Komárek, L. Hornová, A. Horna and J. Churacek, *J. Chromatogr.*, 231 (1983) 299.
322 L. Kozlova, Z. Klavina and L. N. Veselova, *Latv. PSR Zinat.* Akad. Vestis, Kim. Ser., (1983) 187.
323 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 257 (1983) 267.
324 V. E. Medyantsev, A. F. Shushunova and I. I. Stukalina, *Khim. Dreic.*, (2) (1983) 109.
325 G. Crank and J. K. Haken, *J. Chromatogr.*, 245 (1982) 346.
326 V. Gambaro, R. Mariana and E. Marozzi, *J. Anal. Toxicol.*, 6 (1982) 321.
327 J. Riego and A. García-Raso, *J. Chromatogr.*, 360 (1986) 231.
328 W. L. Saxton, *J. Chromatogr.*, 393 (1987) 175.
329 P. A. D'Agostino and L. R. Provost, *J. Chromatogr.*, 331 (1985) 47.
330 P. A. D'Agostino and L. R. Provost, *J. Chromatogr.*, 436 (1988) 399.
331 I. B. Peetre, O. Ellren and B. E. F. Smith, *J. Chromatogr.*, 318 (1985) 41.
332 B. A. Markov, T. I. Rybkina, I. S. Shagrin, V. M. Kopylov, E. A. Kirichenko and L. M. Kubrikova, *Zh. Anal. Khim.*, 36 (1981) 1994.
333 E. Gajewski, M. Dizdaroglu and M. G. Simic, *J. Chromatogr.*, 249 (1982) 41.
334 S. Boneva and N. Dimov, *Chromatographia*, 22 (1986) 271.
335 B. Lin, P. Lu and B. Koppenhoffer, *Sepu.*, 6 (1988) 69.
336 F. Morishita, H. Murakita and T. Kojima, *Bunseki Kagaku*, 34 (1985) 800.
337 A. O. Bender, T. M. Sarkissian and A. M. Allawy, *J. Petr. Res.*, 6 (1987) 153.
338 J. T. Anderson, *J. Chromatogr.*, 354 (1986) 83.
339 H. Tomková, M. Kuchař, V. Rejholec, V. Pacáková and E. Smolková-Keulemansová, *J. Chromatogr.*, 329 (1985) 113.
340 Z. Lin and Y. Hua, *Linchan Huaxue Yu Gongye*, 7 (1987) 46.

341 H. Hendriks and A. P. Bruins, *Biomed. Mass. Spectrom.*, 10 (1983) 377.

342 B. J. Harland, R. I. Cumming and E. Gillings, *Report EUR 10388, Organ. Micropollut. Aquat. Environ.*, Commission of the European Communities, Brussels, 1986, p. 123.

343 J. Chovancová, J. Krupčik, V. Rattey and J. Garaj, *J. Chromatogr.*, 256 (1983) 465.

344 C. Yuan, C. Xiang and H. Long, *Huaxue Xuebaco*, 41 (1983) 248.

345 S. Boneva, *Chromatographia*, 23 (1987) 50.

346 W. Chen, X. Chen and Y. Wang, *Fenxi Huaxue*, 12 (1984) 688.

347 S. Boneva and N. Dimov, *God. Vissh. Khim.-Technol., Burgas Bulg.*, 17 (1982) 97.

348 R. G. Binder and W. F. Haddon, *Carbohydr. Res.*, 129 (1984) 21.

349 V. A. Terentev and M. S. Vigdergauz, *Zh. Anal. Khim.*, 40 (1985) 1670.

350 J. Raymer, D. Wiesler and M. Novotny, *J. Chromatogr.*, 325 (1985) 13.

351 A. Voeckel, J. Szymanowski and J. Beger, *Tenside Surfactants*, 23 (1986) 135.

352 S. Szymanowski, A. Voelkel and H. Swewczyk, *J. Chromatogr.*, 360 (1986) 43.

353 L. Vodicka, J. Triska and J. Hlavaty, *J. Chromatogr.*, 366 (1986) 382.

354 R. V. Golovyna, I. L. Zhuravleva, N. I. Svetlova, M. B. Terenina and S. B. Gutnik, *Zh. Anal. Khim.*, 37 (1982) 294.

355 A. M. Makogon, I. V. Bubentsova, V. L. Trostyanetskaya, L. A. Skripto and I. N. Samosudov, *Zh. Anal. Khim.*, 39 (1984) 353.

356 K. Osmialowski, J. Halkiewicz and R. Kaliszan, *J. Chromatogr.*, 361 (1986) 63.

357 J. Osek, J. Oszczapowicz and W. Drzewiński, *J. Chromatogr.*, 351 (1986) 177.

358 J. Osek, J. Jaroszewska-Manaj, W. Krawczyk and J. Oszczapowicz, *J. Chromatogr.*, 369 (1986) 398.

359 J. Oszczapowicz, J. Osek, K. Ciszkowksi, W. Krawczyk and M. Ostrowski, *J. Chromatogr.*, 350 (1985) 79.

360 P. J. Marriot, J. P. Gill, R. P. Evershed, C. S. Hein and G. Eglinton, *J. Chromatogr.*, 301 (1984) 107.

361 J. Takacs, G. Sandor and A. Vanyi, *Magy. Kem. Foly.*, 90 (1984) 241.

362 D. F. Fritz, A. Sahil and E. sz. Kováts, *J. Chromatogr.*, 186 (1979) 63.

363 G. Anders, K. Anders and W. Engewald, *Chromatographia*, 20 (1985) 83.