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## COMPUTERIZED CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON MIXTURES IN WORKPLACE AIR

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### SUMMARY

The quantitative composition of white spirit vapours in workplace air may differ considerably from the solvent being used, although all components are the same. By calculating the hygienic effect from the threshold limit value (NGV) of each component, a more reliable estimate is obtained of the occupational hazard than by using the NGV for white spirit. In this method the analyses were performed by on-column injection onto a temperature-programmed capillary column. Retention indices based on *n*-paraffins and isooctane were calculated using spline functions. Index tables were established for different hydrocarbon mixtures. The validity of the retention indices was found to be satisfactory, depending on the stability of the column and the possibility of optimizing the indices when replacing one column by another of the same type and dimensions. Comparisons were made with alternative methods for determining the concentration of white spirit vapours in air samples. A polar column was used to check the total content of aromatics.

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### INTRODUCTION

Many attempts have been made in recent years to analyse complex hydrocarbon mixtures, especially petroleum products such as gasoline, naphtha and kerosene<sup>1–8</sup>. Progress in the gas chromatographic (GC) field has been substantial in the 1980s. Fused-silica capillary columns with bonded phases show better temperature and long-term stability than previous columns. The temperature stability of the instruments has been developed, which is of special importance in temperature-programmed gas chromatography. The importance of sound injection techniques has been thoroughly discussed and summarized<sup>9,10</sup>. All this, in combination with the advances in microcomputers and associated software, have created new possibilities for improving upon the analysis of complex mixtures, both qualitatively and quantitatively.

White spirit vapours in workplace air are normally sampled on charcoal tubes. GC analysis is made after carbon disulphide desorption<sup>11</sup>. Calculations are based either on the sum of the peak areas or on a set of peaks in the chromatogram, *e.g.*, *n*-C<sub>9</sub>, *n*-C<sub>10</sub> and *n*-C<sub>11</sub>. A sample of liquid white spirit is used as a standard. Errors may be introduced in this calculation as the composition of vapours sampled often deviates from the standard.

The aim of this work was to make more reliable analyses of white spirit in workplace air by using the separation power of modern capillary columns in a computerized environment.

## EXPERIMENTAL

### *Gas chromatography*

The main GC instrument consisted of a Hewlett-Packard (HP) 5790 with an on-column inlet system ("duck bill" isolation valve) and flame ionization detection (FID). Non-polar columns (50 m  $\times$  0.21 mm I.D.) with 0.50- $\mu$ m cross-linked methylsilicone (HP pretested PONA separation) were used. Runs with carbon disulphide-diluted white spirit were temperature programmed from 45 to about 165°C at 2.0°C/min. The injection volume was 0.25  $\mu$ l or less. The carrier gas was helium at 35 p.s.i., measured linear velocity (methane) 23.8 cm/s at 45°C. FID data: temperature 250°C; flow-rates, hydrogen 36 ml/min, air 253 ml/min and nitrogen (make-up gas) 35 ml/min. Sample injections were made with a 10- or preferably 5- $\mu$ l syringe with a silica needle (100 mm  $\times$  0.17 mm O.D.) (Hamilton 75 RNFS).

A Carlo Erba 4160 chromatograph with a Grob on-column inlet system and FID was used for complementary runs on polar columns (fused silica, 50 m  $\times$  0.32 mm I.D., with 0.57- $\mu$ m CP WAX 57 CB; Chrompack). These runs were temperature programmed from 45 to about 130°C at 1.8°C/min. The injection volume was 0.5  $\mu$ l. The carrier gas was helium at 21 p.s.i., linear velocity 40 cm/s at 45°C. FID data: temperature, 230°C; flow-rates, hydrogen 30 ml/min, air 330 ml/min, nitrogen (make-up gas) 33 ml/min. Sample injections were made with a Hamilton syringe designed for this type of injector.

All columns were protected by moisture filters and the polar column by an additional oxygen trap.

### *Mass spectrometry (MS)*

A Hewlett-Packard HP 5985 quadrupole mass spectrometer equipped with an HP 5840A gas chromatograph was used. Optimum functioning of the jet separator, originally designed for the flow from packed columns, was achieved by addition of make-up helium. Analyses of complex hydrocarbon mixtures were carried out mainly on the non-polar column (PONA). As far as possible, GC parameters in mass spectrometric runs were reproduced from runs with FID. In the mass spectrometer, however, for identification purposes the undiluted solvents (0.5  $\mu$ l) were injected into a split-mode injector (splitting ratio 250:1).

Four different products (*cf.*, Table I) were analysed in the electron-impact mode at 70 eV. Two of these (Varnolene and Exsol D 40) were also analysed by positive-ion chemical ionization using methane as reagent gas.

Complete mass spectra were recorded at a rate of one to two per second. Recorded spectra were studied manually or compared automatically with the built-in library, containing about 35 000 (simplified) spectra. In the case of unseparated peak clusters, mass chromatograms of a few specific ions were compared with the total ion chromatogram. In this way, it was possible to find the position and group identity of the different substances making up the cluster. In those instances retention times were roughly estimated for each of the components. This made it possible to create large

enough local windows, even if another component in the mixed peak dominated (see below).

### Data handling

A reporting integrator, HP 3390A with RS-232C interface lacking handshaking lines, transmitting rate 1200 baud, was used to collect raw data from the GC instrument. Normal integration parameters with the main GC instrument (HP 5790) at 1 V output signal were ATT 1, PK WD 0.04 min, THRSH -2, AR REJ 0. A Swedish ABC-1600 computer (Luxor) with ABCenix operating system (Xenix-like) was used. The primary memory was 1 Mbyte, and a 13-Mbyte Winchester disk was used for mass storage. The Xenix software package included "The programmers workbench", containing a routine for spline function calculations. The programs were written in Basic II (DIAB AB) with possibilities for structured programming by using its multiline functions<sup>12</sup>. From the Basic program, a call was made to the spline program (written in C) that computed the spline function.

The integrator transmitted the report as an ASCII string to the external computer, where it was stored in a file for further use. This file was used for making index or retention time tables by the addition of missing data, *e.g.*, NGV, name, formula. A spline function consisting of cubic polynoms was used. The reference peaks were used as knots in the spline curve (see *Creation of index tables and window handling*). The number of knots used was given by the number of reference peaks found in the sample. At least three knots are needed, but normally seven were used.

### Chemicals and solutions

Carbon disulphide was Baker analyzed grade from J. T. Baker (Deventer, The Netherlands) was used as a desorption agent and as the solvent for standards. Isooctane (puriss p.a.) and tridecane (puriss., standard for gas chromatography), both from Fluka (Buchs, Switzerland) were used as internal standards. Other solvents used for identification purposes were obtained from different manufacturers.

Hydrocarbon solvents were obtained from different oil companies. Products from Esso Chemicals were selected for detailed study and the creation of index tables (Table I).

TABLE I  
DATA FOR PRODUCTS USED FOR INDEX TABLE CREATION

Product <sup>a</sup>	Aromatic content (%, w/w)	Boiling range (°C)	NGV <sup>b</sup> (mg/m <sup>3</sup> )
Varnolene	20	152-195	500
Exsol D 40	<1	159-193	- <sup>c</sup>
Solvesso 100	99	165-179	120
Solvesso 150	99	190-209	120

<sup>a</sup> Typical analysis data published by Esso Chemicals.

<sup>b</sup> The threshold limit values stated are the standard 8-h time-weighted averages published in AFS 1987:12 by the National Swedish Board of Occupational Safety and Health<sup>13</sup>.

<sup>c</sup> No NGV exists.

Separate solutions were prepared from a number of pure hydrocarbons by weighing 20  $\mu$ l of each into 1.5 ml of carbon disulphide in a 1.5-ml screw-capped vial with PTFE-faced discs, which were fitted tightly during the preparation. These solutions were used for the determination of FID response factors. The internal standard was *n*-C<sub>13</sub> with isooctane acting as a test compound (to check the success of injection). Immediately before use the solutions were diluted with carbon disulphide to a concentration of about 200 ppm (v/v).

Charcoal tubes (100 + 50 mg) were obtained from different sources.

### Sample preparation

Hydrocarbons trapped in charcoal tubes during sampling were desorbed with 1 ml of carbon disulphide into 7- or 3.5-ml screw-capped vials. The solutions were tested for compounds with the same retention time as the internal standards (*n*-C<sub>13</sub> and isooctane). Internal standard (1 ml of a 100 ppm solution), was then added to the sample vials. The vials were shaken for about 30 min.

## RESULTS AND DISCUSSION

Extensive experience in analysing workplace air concentrations of white spirit and other complex hydrocarbon mixtures has shown us that the liquid giving rise to the air contamination seldom shows the same GC pattern as the gaseous phase. This can easily be demonstrated experimentally. A small amount of white spirit was placed on a filter-paper in a shallow dish and an air sample was taken above the evaporating solvent at different times. Results are given in Table II, showing the normalized *n*-C<sub>9</sub>, *n*-C<sub>10</sub> and *n*-C<sub>11</sub> GC peak areas. Practical experience and the test in the laboratory suggested the work presented in this paper.

### Hygienic effect

The hygienic effect of the contaminants in an air sample is defined as the sum of the ratios between the concentration and threshold limit value (NGV) of each component<sup>13</sup>. This is valid assuming that each component has a similar effect on man. When the sum of the ratios exceeds unity, the NGV of the mixture is exceeded.

$$\text{Hygienic effect} = \frac{C_1}{T_1} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \dots + \frac{C_n}{T_n}$$

TABLE II  
EVAPORATION OF WHITE SPIRIT

The table shows normalized concentration values (*C*<sub>10</sub> = 100) at different times after the start of evaporation.

Sample	<i>n</i> -C <sub>9</sub>	<i>n</i> -C <sub>10</sub>	<i>n</i> -C <sub>11</sub>
Liquid solvent	37	100	45
Gas, 0 h	114	100	15
Gas, 1.5 h	17	100	27
Gas, 4 h	0	100	588

where  $C_i$  = concentration of component  $i$  ( $i = 1, 2, 3, \dots, n$ ) and  $T_i$  = threshold limit value of  $i$ .

In most instances NGVs refer to pure substances. In this context, however, special interest is attached to NGVs assigned to complex hydrocarbon solvents. When calculating such NGVs, the solvent (*e.g.*, white spirit) is treated as a mixture of a very limited number of typical components. As is obvious from this study, the NGV value (and hence the hygienic effect), when calculated from all elements in an air sample contaminated by hydrocarbons, may deviate considerably from that obtained by the simplified method used up to now.

#### *Creation of index tables and window handling*

The GC of white spirit, even with highly efficient columns, produces very complex chromatograms. The retention index calculation should give a reproducibility of the indices of better than 0.5 index unit.

Commercial solvents based on petroleum contain a certain range of paraffinic, cycloparaffinic and aromatic hydrocarbons. In order to create reference index tables, a set of representative products was selected from the range available from Esso Chemicals (*cf.*, Table I). Samples of undiluted solvent were analysed by GC-MS and the components were identified or classified according to carbon number and structure. In this way 234 different hydrocarbons were found in Varnolene and 255 in Exsol D 40. The content of olefinic substances is usually low and for this reason, and because of the difficulty in distinguishing them from the cycloparaffins, they were classified as such. The results were transferred to corresponding chromatograms obtained with FID. Retention times provided basic data for the index calculations with  $C_8$ - $C_{12}$  *n*-alkanes normally occurring in white spirit samples as reference points. Isooctane and *n*-tridecane were added, acting both as reference points and internal standards. The cubic spline interpolation method<sup>14,15</sup> was chosen for these calculations. A typical spline curve showing retention time *versus* index is shown in Fig. 1.

Index tables were created for Varnolene, Exsol D 40 and a mixture of Solvesso 100 and Solvesso 150 (1:1). Retrieving a given compound in a sample indicates a certain amount of agreement between sample and reference indices. Normally, the index was allowed to vary within the limits of a  $\pm 0.25$  index unit window centred on

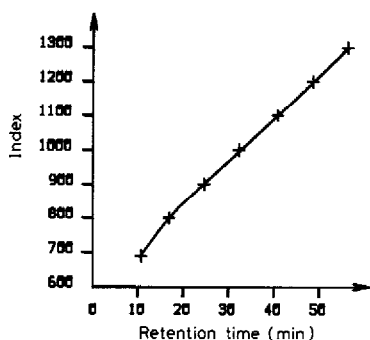


Fig. 1. A typical spline curve where  $C_8$ - $C_{13}$  *n*-alkanes and isooctane are used as reference points. The index value of isooctane was initially calculated in a run using *n*-hexane and *n*-heptane as reference points in addition to the regular *n*- $C_8$ -*n*- $C_{13}$  standards.

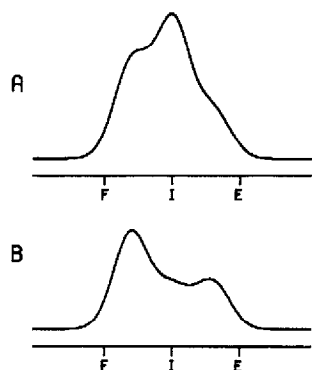


Fig. 2. A case with three compounds in different concentration ratios. (A) Portion of the chromatogram of the standard used for the creation of the index table. The complex peak is assigned an index I due mainly to the contribution of the component eluted near the maximum of the peak cluster. (B) Hypothetical sample chromatogram where the latter component is present in a much lower concentration relative to the others. In this instance none of the components become classified as "not identified", depending on the expansion of the window before (F) and after (E) the index (I) assigned to the peak complex.

Index	Rtime	Compound	Group	Formula	NGV	Note
...	...		.	...	...	...
945.95	28.036	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	
947.01	28.123	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	
947.01	28.123	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	
949.61	28.337	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	FX
949.61	28.337	C <sub>9</sub>	A	C <sub>9</sub> H <sub>12</sub>	120	
951.76	28.514	C <sub>9</sub>	A	C <sub>9</sub> H <sub>12</sub>	120	
951.76	28.514	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	EEX
956.09	28.871	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	F
956.09	28.871	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	
957.59	28.994	1,3,5-Trimethylbenzene	A	C <sub>9</sub> H <sub>12</sub>	120	
957.59	28.994	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	E
960.46	29.231	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	F
960.46	29.231	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	
960.46	29.231	C <sub>10</sub>	N	C <sub>10</sub> H <sub>20</sub>	500	E
962.25	29.378	C <sub>10</sub>	P	C <sub>10</sub> H <sub>22</sub>	500	
...	...	...	.	...	...	...

Fig. 3. Example from an index table. NGV = Threshold limit value; X = excluded from the calculation (see text); E, F = the window is opened one additional index unit behind (E), or in front of (F) the nominal 0.5 unit slot centred on the normal peak maximum; EE = two index units expansion. A = Aromatics; P = alkanes; N = cycloalkanes. Rtime = Retention time in min.

the peak maximum. However, in many instances two or more components merge, forming an irregular peak. Often, such a peak is dominated by one compound governing the position of the peak maximum. In order not to lose such a peak, should the dominating substance be missing or occur in only minute amounts, the window is extended locally by the use of special markers (Figs. 2 and 3). Therefore, depending on the position of the underlying compounds, the index window of an irregular peak could be widened by one or two index units.

In some mixed peaks a small trace of a compound with a different NGV was found. It was considered reasonable to exclude such peaks (see Fig. 3, "X") in order not to influence the calculated hygienic effect (see *Field tests*).

In order to test the applicability of the index tables, a number of white spirit products from different suppliers were analysed (Table III). It is evident that the various samples are very much alike qualitatively, as can be seen from the amounts of unidentified substances shown in the table (see also Fig. 4).

Probably, because of the difficulty in defining the true baseline during the integration of the very complex chromatograms produced by white spirit, the total amount registered as "identified" and "unidentified" in Table III is less than the amount actually injected. The yield was found to be about 90% when analysing normal white spirit (*ca.* 20% aromatics) and about 85% for the low aromatic mixture. Better results would be expected by the use of microcomputer-based integration programs not available at the time this work was done.

### Columns

A crucial point in this context has been the choice of stationary phase. Squalane has often been used because of its non-polarity<sup>1,2,7,16,17</sup>. However, squalane cannot be

TABLE III  
WHITE SPIRIT FROM DIFFERENT OIL COMPANIES

Column: non-polar (and polar for aromatic compounds in parentheses; see Experimental). No. 1 was used to produce an index table used for mixtures 1-5. Mixtures 6-8 are declared as low aromatic and the estimation was made with an index table of a hydrocarbon mixture (No. 6) of same type. The window was  $\pm 0.25$  I, except for the polar column, where it was  $\pm 2.5$  s. *n*-C<sub>13</sub> was used as an internal standard.

No.	Identified (mg)	Unidentified (mg)	Aromatic compounds (mg)	<i>n</i> -C <sub>9</sub> - <i>n</i> -C <sub>11</sub> (%)
1	6.79	0.07	1.32-2.12 (1.65)	27.0
2	6.76	0.12	1.22-2.05 (1.48)	26.3
3	6.54	0.18	1.10-1.95 (1.12)	22.5
4	6.30	0.26	1.05-1.93 (1.12)	22.3
5	6.59	0.07	1.22-2.05 (1.53)	24.7
6	6.64	0.07	-	27.0
7	6.24	0.15	-	30.5
8	6.50	0.09	-	28.8

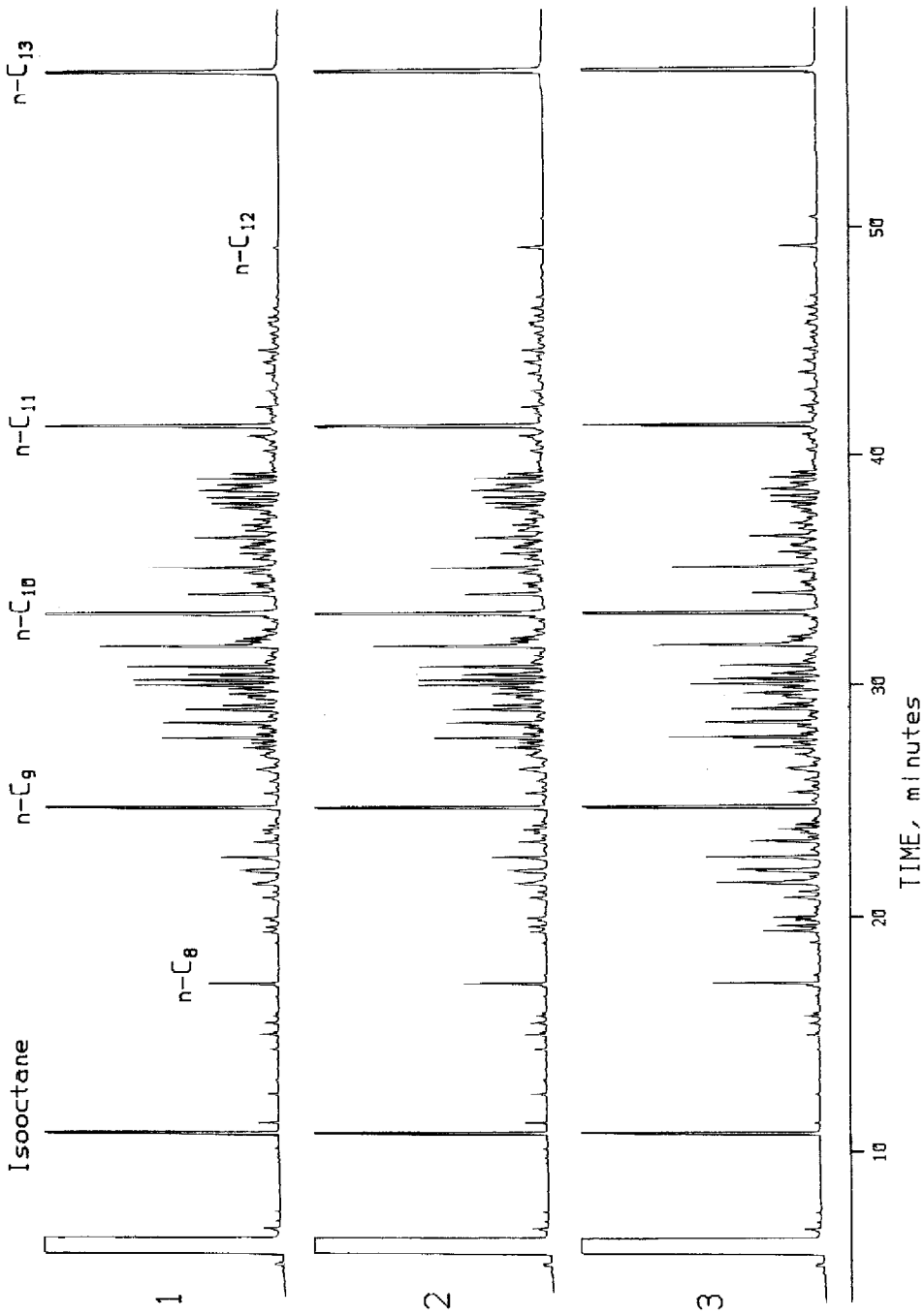


Fig. 4. Chromatograms of white spirit from three different sources containing ca. 20% aromatic compounds. Column (non-polar): 50 m  $\times$  0.21 mm I.D., 0.50- $\mu$ m cross-linked methylsilicone. Oven programme: 45 to 165°C at 2°C/min.



used above 100°C, leading to long analysis times. The advent of the cross-linked methylsilicone phase bonded to the inner surface of fused-silica capillary columns was a great advantage in this work. This phase is nearly as non-polar as squalane but can be used up to and above 300°C.

Both long- and short-term reproducibility is of great importance when using index systems<sup>15</sup>. In this work, the temperature is normally programmed to about 165°C. Further, the volumes injected are as small as 0.25  $\mu$ l at a starting temperature of 45°C. These conditions guarantee a long column life. From the example shown in Table IV, it can be seen that the indices are nearly the same over a 16-month period of use. The choice of a pretested commercial product manufactured especially for hydrocarbon mixtures makes it possible to ensure a future supply of columns differing so little from each other that the index tables will remain valid.

Knöppel *et al.*<sup>15</sup> discussed the possibility of changing one or more parameters, *e.g.*, column inlet pressure, temperature programming rate or column dimensions, to obtain appropriate index adjustments. From Table IV, it is clear that the indices from a new column (No. 2) can be adjusted by means of the column inlet pressure so that they will agree with the indices from column No. 1, used when preparing the index tables. Changing the inlet pressure for column 2 from 34.5 p.s.i., which corresponds to 35.0 p.s.i. in column 1 for the same flow-rate, to 33.5 p.s.i. gives more acceptable indices. As expected, the improvement is obvious for the aromatic compounds, but the cycloparaffin indices also show better agreement with previous values.

An alternative is to use a polar column for the analysis of white spirit. The peaks after the unresolved peak consisting of *o*-xylene and *n*-dodecane are aromatics and the peaks before are paraffins and cycloparaffins. This is apparent from Fig. 5, where a low aromatic mixture (<0.5% aromatics) was run for comparison. Drawbacks are,

TABLE IV  
INDEX VERSUS RETENTION TIME

Long-term stability of a non-polar column (column 1) as measured during a 16-month period ( $T_2 = T_1 + 16$  months). Values obtained on new column (column 2) with (33.5 p.s.i.) and without (34.5 p.s.i.) column inlet pressure optimization. Injected solution: 1000 ppm Varnolene + 25 ppm each of isooctane and *n*-tridecane (Varnolene was the same as used for the index table). A = aromatics; P = alkanes; N = cycloalkanes.

Type	Compound	Column 1				Column 2			
		$T_1, 35.0$ p.s.i. He		$T_2, 35.0$ p.s.i. He		Run 1, 34.5 p.s.i. He		Run 2, 33.5 p.s.i. He	
		$t_R$ (min)	$\Delta I$	$t_R$ (min)	$\Delta I$	$t_R$ (min)	$\Delta I$	$t_R$ (min)	$\Delta I$
A	C <sub>8</sub>	22.747	881.62	+0.009	+0.08	-0.026	-0.17	+0.315	-0.07
	C <sub>9</sub>	31.049	982.52	-0.003	+0.04	-0.003	-0.19	+0.381	-0.03
	C <sub>10</sub>	38.091	1067.92	-0.008	+0.04	+0.022	-0.22	+0.427	-0.05
P	C <sub>9</sub>	22.078	873.35	+0.003	-0.01	-0.015	-0.02	+0.314	-0.01
	C <sub>10</sub>	29.378	962.25	-0.006	-0.02	+0.006	-0.02	+0.373	+0.01
	C <sub>11</sub>	37.558	1061.43	-0.012	-0.02	+0.035	-0.04	+0.428	0.00
N	C <sub>9</sub>	19.487	839.87	+0.009	0.00	-0.024	-0.08	+0.289	-0.03
	C <sub>10</sub>	31.262	985.11	-0.007	-0.02	+0.006	-0.10	+0.389	+0.04
	C <sub>10</sub>	35.146	1032.15	-0.010	-0.01	+0.016	-0.15	+0.414	+0.02

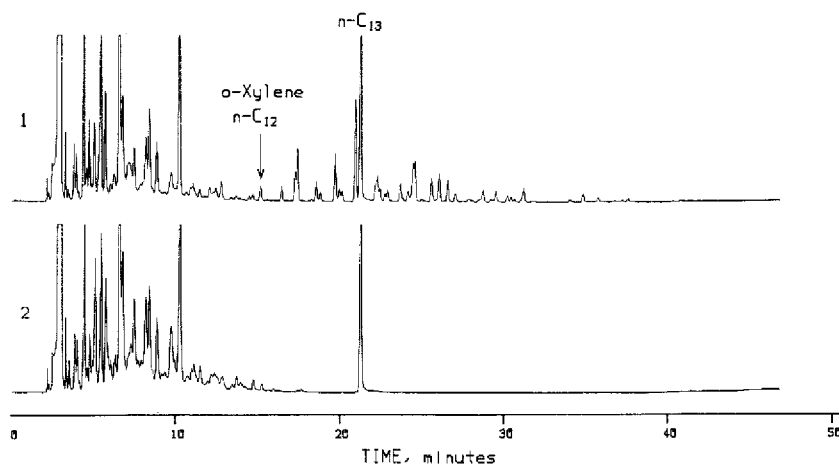


Fig. 5. Chromatograms of white spirit containing (1) about 20% and (2) about 0.5% aromatics. Column (polar): 50 m  $\times$  0.32 mm I.D., 0.57- $\mu$ m CP-WAX 57 CB. Oven programme: 45 to about 130°C at 1.8°C/min. These chromatograms illustrate that only aromatics elute after the peak containing dodecane and *o*-xylene. *n*-Tridecane is added as an internal standard.

however, the uncertainty in the integration of the badly resolved peaks at the beginning and the difficulty in determining the identity of the peaks.

The polar column was used as a complement, however, as it gave the possibility of determining the aromatic hydrocarbon content more accurately. It is difficult to make polar columns with identical properties and they are more apt to degenerate. Therefore, it was not meaningful to make permanent index tables. Instead, retention time tables for the aromatics were drawn up from integrator reports when needed.

#### *On-column injection*

The on-column injection technique discussed by many workers<sup>9,10,18,19</sup> has some advantages for this type of analysis. One is that discrimination effects can be reduced if the technique is handled correctly. It is evident from Table VIII that the amount of white spirit differs very little when calculated with isooctane as internal standard, eluted in the beginning of the chromatogram, or with *n*-tridecane, eluted at the end.

Another advantage is, of course, the increased sensitivity over that of the split technique. To obtain the highest possible column efficiency, a column was used with an I.D. of only 0.21 mm, which is less than normally recommended in on-column injection. A consequence of this is that the solvent effect deteriorates and the peaks become observably broadened in the latter half of the chromatogram when more than about 0.30  $\mu$ l is injected. This volume has so far been sufficient for the analysis but, if it became necessary to inject a larger volume to increase the sensitivity, it might be advisable to connect a short uncoated column prior to the coated column<sup>10</sup>. When the inner diameter is as small, as used here, it is important to centre the column, otherwise it can be difficult to introduce the needle, resulting in poor injections.

Larger volumes can be injected onto the polar column without broadening the aromatic peaks (for which this column was used) because the inner diameter is larger.

in spite of the fact that carbon disulphide is not well suited to this column. The choice of carbon disulphide is possibly not the best, even for the non-polar column. However, it is an efficient desorption agent for hydrocarbons adsorbed on charcoal. The injections were made without any secondary cooling with a column start temperature of 45°C, just below the boiling point of carbon disulphide (46°C). Prior to the injection, the solvent was drawn back from the needle to avoid the loss of part of the volume and the needle was then cleaned. The injections were made rapidly, after which the needle was quickly withdrawn.

#### *Choice of reference points in spline function calculations*

From Table V, the necessity for using the same reference points in the spline function for the sample as for the index table is evident. A typical example is shown in run 2, where white spirit peaks totalled 99.1% of the area registered by the integrator at window width 1.0 index unit (I). Omitting, for example, the point  $n\text{-C}_8$  in the sample spline function but not in the index table gives only 80% recovery. Under such conditions, there is also reason to question the peak identities. These are of utmost importance for the calculation of the hygienic effect. These errors become larger with smaller windows. If, on the other hand,  $n\text{-C}_{12}$  is omitted in the sample spline calculation, the result is considerably better, if not acceptable, owing to the fact that the spline curve is more linear in this region. Even if only isooctane,  $n\text{-C}_{10}$  and  $n\text{-C}_{13}$  are used as reference points, the results are fairly good, provided that the windows are not set too narrow and the same reference points are used, in spite of the fact that the indices differ by several units from those calculated with the use of all reference points. In this instance, however, it is of special importance to keep the injection volumes as similar as possible to those used when constructing the index tables in order not to affect the retention times of early eluting peaks.

Table V also illustrates the inferior results obtained with narrow windows in run 1 (unoptimized carrier gas flow; *cf.*, Table IV), even when using all reference points.

TABLE V

#### PEAKS-FITTING INDEX TABLE CALCULATED BY SPLINE FUNCTIONS USING DIFFERENT SETS OF REFERENCE POINTS

Results are shown for three different windows. Reference points  $n\text{-C}_8\text{--}n\text{-C}_{12}$  are provided by  $n$ -alkanes normally occurring in white spirit. The runs are the same as in Table IV (column 2). Index table and sample runs were made on different occasions on two columns of the same kind.

<i>Set of reference points used in</i>		<i>Peak area (% of total registered)</i>					
		<i>Run 1</i>			<i>Run 2</i>		
<i>Index table</i>	<i>Sample table</i>	<i>1.0 I<sup>a</sup></i>	<i>0.5 I<sup>a</sup></i>	<i>0.2 I<sup>a</sup></i>	<i>1.0 I<sup>a</sup></i>	<i>0.5 I<sup>a</sup></i>	<i>0.2 I<sup>a</sup></i>
All	All	99.1	97.4	72.8	99.1	99.0	97.8
All	Omitted: $n\text{-C}_8, n\text{-C}_{12}$	—	—	—	73.1	45.2	37.9
All	All except $n\text{-C}_8, n\text{-C}_{12}$	—	—	—	99.1	99.0	97.9
All	Omitted: $n\text{-C}_8$	—	—	—	80.0	52.9	40.6
All	Omitted: $n\text{-C}_{12}$	—	—	—	97.6	95.4	82.0
	3 reference points (isooctane, $n\text{-C}_{10}, n\text{-C}_{13}$ )	—	—	—	99.1	99.0	76.5

<sup>a</sup> Window (index units).

### Comparison with linear regression

Table VI shows the identified part of the peak area (for the same runs as shown in Tables IV and V) with peaks identified by linear regression using retention times. The window here was 0.04 min (0.50 I). With only one reference point (*n*-C<sub>13</sub>) the whole curve is corrected by an offset equal to the difference between the retention times for that point in the table and in the real sample.

From Table VI, it is clear that using linear regression in fitting the retention times of sample peaks to the standard retention time table leads to a lower recovery than using the spline method discussed above. This is particularly evident in run 1 (flow in the new column not adjusted) and when fewer reference points are used in the calculations. Again, the low recovery is indicative of considerable errors in peak identification.

### FID relative response factors

In the early 1960s, Ettre<sup>20</sup> discussed data published on the FID relative responses of C<sub>5</sub>–C<sub>10</sub> hydrocarbons. He found variations of up to ±4%, with some exceptions. Miller and Ettre<sup>21</sup> studied the relative responses of a few typical hydrocarbons and reported similar variations for saturated aliphatics but higher responses for three C<sub>7</sub>–C<sub>8</sub> aromatics studied.

It was deemed necessary to confirm these earlier findings using on-column injection onto capillary columns as described above. Table VII gives results for some different individual hydrocarbons. The data were corrected for impurities estimated by separate runs on the non-polar column.

The response factor relative to *n*-tridecane (1.00) is defined by

$$f_{r(i)} = \frac{A_i/m_i}{A_{st}/m_{st}}$$

where  $A_i$  = peak area of compound *i*,  $m_i$  = amount of compound *i*,  $A_{st}$  = peak area of *n*-C<sub>13</sub> standard and  $m_{st}$  = amount of *n*-C<sub>13</sub> standard (all amounts corrected for impurities). The results in Table VII are averages of one or more runs of at least two different weighings. The same solutions were used for both instruments.

In the light of literature data<sup>20–22</sup> and results of this study, it is apparent that the response factor can be accepted as being equal to 1 in this kind of analysis. The aromatics examined in Table VII give up to 5% higher responses than the others.

TABLE VI

RUNS IN TABLE V CALCULATED WITH LINEAR REGRESSION USING RETENTION TIME DATA

Reference points	Peak area (% of total registered)	
	Run 1	Run 2
All points	75	90
Isooctane, <i>n</i> -C <sub>13</sub>	26	16
<i>n</i> -C <sub>13</sub>	37	40

TABLE VII  
FID RELATIVE RESPONSE FACTORS OF HYDROCARBONS

Compound	Purity (%)	Formula	Relative response factor	
			Instrument 1 <sup>a</sup>	Instrument 2 <sup>a</sup>
Isooctane	100.0	C <sub>8</sub> H <sub>18</sub>	1.00	—
<i>n</i> -Octane	99.9	C <sub>8</sub> H <sub>18</sub>	1.00	—
<i>n</i> -Butylcyclohexane	99.6	C <sub>10</sub> H <sub>20</sub>	1.01	1.01
<i>n</i> -Decane	99.6	C <sub>10</sub> H <sub>22</sub>	1.00	—
<i>n</i> -Butylbenzene	99.4	C <sub>10</sub> H <sub>14</sub>	1.04	1.05
1,2,3,4-Tetramethylbenzene	97.5	C <sub>10</sub> H <sub>14</sub>	1.03	1.03
1,2,3,5-Tetramethylbenzene	99.0	C <sub>10</sub> H <sub>14</sub>	1.03	1.04
1,2,4,5-Tetramethylbenzene	99.9	C <sub>10</sub> H <sub>14</sub>	1.04	1.05
Phenylcyclohexane	97.0	C <sub>12</sub> H <sub>16</sub>	1.04	1.04
<i>n</i> -Tridecane	99.5	C <sub>13</sub> H <sub>28</sub>	1.00 <sup>b</sup>	1.00 <sup>b</sup>

<sup>a</sup> Instrument 1: Hewlett-Packard 5790, non-polar column. Instrument 2: Carlo Erba 4160, polar column.

<sup>b</sup> Standard, 1.00 by definition.

Assuming that this holds for all white spirit aromatics and that the content of aromatics is 20% (w/w) as in normal white spirit, the error will be less than 1% on a weight basis when using the NGV values in Table I. In hygienic effect calculations using NGV values for individual components, the error will be higher. This may be taken into consideration by the use of a correction factor.

#### Field tests

Air samples taken by charcoal adsorption in different workplaces were analysed by the spline index method. The results are given in Table VIII. In this table, comparison is also made with the method using a set of larger peaks in the standard (for samples 1–6 Varnolene and for samples 7–9 Exsol D40), namely the C<sub>9</sub>–C<sub>11</sub> *n*-paraffins, as a measure of calculating the total amount of hydrocarbons from the same set of peaks in the samples. As the concentration of the C<sub>9</sub>–C<sub>11</sub> *n*-paraffins may vary considerable (*cf.*, Table III), it is obviously difficult to choose a suitable standard. In the spline index method described here, this difficulty is circumvented as all peaks fitting the index table with the window used (0.5 I) are taken into consideration. As can be seen, only minute amounts fall outside the window (“unidentified”). This holds for moderate concentrations. Sample No. 2 is an example of column overloading.

The hygienic effect is presented as a range rather than a single value because, in certain instances, hydrocarbons with different NGVs fall within the same window. The lower limit is found by using the higher NGV in all such instances and *vice versa*. The most important case is, of course, the coincidence of aromatic and aliphatic compounds. In certain instances, however, this rule must be abandoned. For example, white spirits, other than those very high in aromatics, show two dominating peaks, *n*-decane and *n*-undecane. Both are contaminated by negligible amounts of aromatics. These must be disregarded in order not to introduce very large errors in the calculation (see comments on Fig. 3).

A third method often applied to the calculation of the amount of hydrocarbons

TABLE VIII  
RESULTS OF AIR SAMPLE ANALYSES

No.	Internal standard	Identified (mg)	Unidentified (mg)	Hygienic effect		Aromatic compounds (mg) <sup>a</sup>	Total amount (mg) <sup>b</sup>
				Individual peaks	Total area		
1	<i>n</i> -C <sub>13</sub>	0.27	0.02	0.55–0.70	0.45	0.05–0.08	0.21
	Isooctane	0.27	0.02	0.54–0.70	0.45	0.05–0.08 (0.05)	
2	<i>n</i> -C <sub>13</sub>	5.31	3.38	1.49–1.95	1.36	0.84–1.51 (1.43)	6.57
3	<i>n</i> -C <sub>13</sub>	2.04	0.05	13.60–17.10	11.37	0.36–0.58	1.59
	Isooctane	2.03	0.05	13.54–17.03	11.33	0.36–0.58 (0.33)	
4	<i>n</i> -C <sub>13</sub>	0.55	0.02	0.12–0.16	0.10	0.11–0.17	0.46
	Isooctane	0.54	0.02	0.12–0.15	0.09	0.10–0.17 (0.10)	
5	<i>n</i> -C <sub>13</sub>	0.96	0.02	1.29–1.66	1.14	0.16–0.28	0.78
	Isooctane	0.90	0.02	1.21–1.56	1.07	0.15–0.27 (0.12)	
6	<i>n</i> -C <sub>13</sub>	0.32	0.01	0.20–0.26	0.16	0.05–0.09	0.24
	Isooctane	0.32	0.01	0.20–0.26	0.16	0.05–0.09 (0.06)	
7	<i>n</i> -C <sub>13</sub>	0.30	0.06	0.08–0.09	—	—	0.31
	Isooctane	0.31	0.06	0.09–0.09	—	—	
8	<i>n</i> -C <sub>13</sub>	1.77	0.03	1.33–1.46	—	—	1.65
	Isooctane	1.79	0.03	1.34–1.47	—	—	
9	<i>n</i> -C <sub>13</sub>	0.62	0.02	0.35–0.39	—	—	0.54
	Isooctane	0.63	0.02	0.36–0.39	—	—	

<sup>a</sup> Figures in parentheses refer to polar column runs.

<sup>b</sup> Calculated with C<sub>9</sub>–C<sub>11</sub> *n*-alkanes (see text).

in the samples is based on the use of the total area of all peaks. The hygienic effect thus found using the white spirit NGV (500 mg/m<sup>3</sup>) is shown for comparison. All these values are lower than the lower limit of the range found. No figures are shown for the samples low in aromatics as no NGV exists. A drawback with the total area method is the error introduced if substances other than white spirit hydrocarbons are present in the samples. The chances are that such “foreign” peaks will fall outside the windows of the spline index method and thus become characterized as “unidentified”.

In addition, Table VIII shows the complete lack of discrimination effects due to boiling-point differences; the same results are found with isooctane and *n*-tridecane as internal standard. Not shown in this table is the good repeatability between injections. In no instance did the results from two runs differ more than  $\pm 2\%$  from their mean value.

## CONCLUSION

This study has shown the possibility of calculating the hygienic effect of white spirit in workplace air using spline functions in calculating retention indices. The

method, general in nature, can be applied to many other analytical tasks dealing with complex analytes. In this context it should also be mentioned that this possibility of obtaining better resolution and identification of complex workplace air contaminants is a prerequisite for the estimation of occupational hazards based on individual NGVs.

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