
Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept

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Abstract

Equations are given for relating flame ionization detector relative response factors to the effective carbon number (ECN) of neat and derivatized components. The ECN approach can be used for calculating relative response factors in cases where pure materials are not available for detector calibration. Examples of this approach are given for the analysis of polycyclic aromatic hydrocarbons and oxygenated organics in neat form, alcohols and acids as the trimethylsilylated derivatives, and carbohydrates as the trimethylsilyl-oxime derivatives.

Introduction

The ability to calculate response factors for analyses utilizing the flame ionization detector (FID) is of fundamental importance in gas chromatographic (GC) methods development. When relative response data is obtained for a new compound (in either the neat or derivatized form), it is desirable to have some means to calculate what the response should be for comparison with the experimentally determined value. Since the experimentally determined factor is dependent on the purity of the compound, the completeness of reaction (if a derivatization step is used), possible decomposition on injection, and adsorption by the column, relative response factors (area multiplying factors) may be significantly different from that which should be obtained. Although literature values may be found for compounds of similar structure, these may not be applicable to the new compound.

The concept of the effective carbon number (ECN) was introduced many years ago (1) in studies to explain the observed flame ionization responses obtained from the analysis of isomeric or homologous series of organic compounds. Other workers (2-8) have presented and tabulated data on the contribution of different functional groups to the ECN. In spite of its potential usefulness, the calculation of the ECN does not appear to have been widely used in recent years. It is the intent

of this paper to show how the ECN has been used for column evaluation, as a check on experimentally determined response factors for neat and derivatized compounds, and for the calculation of response factors for compounds which cannot be obtained in pure form.

Experimental

All of the data were obtained using Model 3700 gas chromatographs (Varian) and a Model 3353-E lab automation system (Hewlett-Packard). Two columns were used. The first was a 10-m Series 530 μ methyl silicone column (Hewlett-Packard) with hydrogen carrier gas at a linear velocity of 30 cm/sec. The injection port of the instrument utilized the fused silica lined direct-injection insert (Hewlett-Packard) and was operated at 250° or 300°C (PAHs only). The hydrogen and air flows were 30 and 300 ml/min, respectively, as specified by the manufacturer. Make-up gas (He) was added before the flame ionization detector. The second column was a 50-m $\times$ 0.22-mm i.d. WCOT fused silica column coated with XE-60-S-valine- α -phenylethylamide (Chrompack) operated in the split mode, with a split ratio of 50:1. Helium was used as the carrier gas at a linear velocity of 26 cm/sec. This column is normally used for the analysis of optical isomers. It gave excellent results for the carbohydrate-trimethylsilyl (TMS)-oximes and polycyclic aromatics through fluoranthene. The retention times for aromatics higher boiling than fluoranthene are excessively long at the safe maximum operating temperature of 180°C with this column.

The FID electrometers were run at a sensitivity of E-9 or E-10 amp/mV with the methyl silicone column (depending on standard concentration) and at E-11 amp/mV with the chiral column. The chromatograms were displayed on 1-mV strip-chart recorders (Varian or Hewlett-Packard). Signal integration via the lab automation system was collected at 4 Hz. Appropriate baseline events were included in the system methods to assure baseline corrected peak areas. Relative response data was calculated automatically by the lab automation system from calibration tables in the system methods. In the analysis of the oximated derivatives, some of the carbohydrates were resolved into peaks for the syn- and anti-forms; the sum of the peaks was used for

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calculation of the response factors and ECNs.

Analysis of the same standard solution on each of the columns gave component area counts consistent with the differences in electrometer sensitivities and the nominal 50:1 split ratio. Although both direct and cold on-column injection would be more precise methods for introducing known absolute amounts of solutes onto the column, the amounts of components shown in Table VI as being injected onto the column are believed to be reasonably accurate. In any event the amount on column is less than by direct injection of the same standard and was intended to illustrate the experimental observations on the relative response factors for the polycyclic aromatic hydrocarbons as discussed below.

Figures 1 and 2 illustrate the resolution of a qualitative mixture of polycyclic aromatic hydrocarbons on the two columns used. On the Series 530 μ column, elution of the aromatics through 2,2'-binaphthyl can be achieved in less than 15 min under these conditions.

The chemicals used were from various sources and were corrected for purity where indicated by the supplier. The polyols and carbohydrates were obtained from Sigma Chemical, while all other chemicals were from Eastman Chemicals and Aldrich Chemical Co.

The trimethylsilylated and trimethylsilylated-oxime derivatives of the polyols and carbohydrates were prepared from pyridine

solutions as previously described (9). Acetophenone was quantitatively converted to the oxime derivatives under the same conditions. It was necessary to react benzophenone at 60°C overnight or at 100°C for over 30 min to achieve quantitative conversion to the oximated derivatives. The polycyclic aromatic hydrocarbons were prepared in toluene solution at an initial concentration of about 5 $\mu\text{g}/\mu\text{l}$. This stock solution was further diluted to achieve the lower concentrations.

Results and Discussion

For the purposes of this paper, a relative weight response factor (multiplier) will be defined by:

$$F(R\text{-wt}) = \frac{\text{area counts for ref.} \times \text{wt. of comp.}}{\text{area counts for comp.} \times \text{wt. of ref.}} \quad \text{Eq. 1}$$

This equation is based on a response factor of 1.0 for the reference compound by definition. On this basis, the numerical value of the relative response factor is the weight of the component necessary to produce the same response (area counts) as the reference component. The reciprocal of the relative response factor is the relative sensitivity of the FID to equal

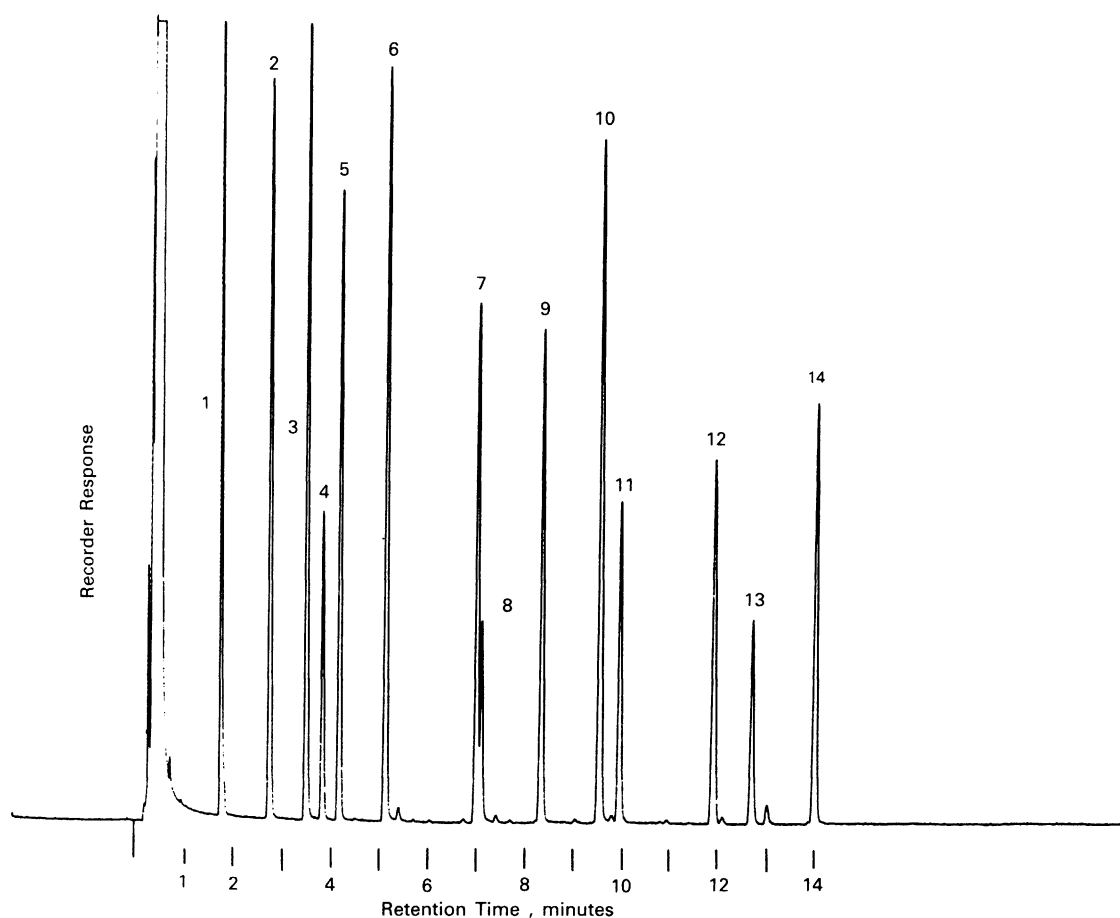


Figure 1. Chromatogram of polynuclear aromatic hydrocarbons on a Series 530 μ column. Peak identification: 1=naphthalene; 2=tridecane; 3=2,6-dimethylnaphthalene; 4=acenaphthylene; 5=acenaphthene; 6=fluorene; 7=phenanthrene; 8=anthracene; 9=1-methylphenanthrene; 10=fluoranthene; 11=pyrene; 12=1,1'-binaphthyl; 13=chrysene; 14=2,2'-binaphthyl. Chromatographic conditions: temperature program at 100°C increased at 10°/min to 250°C; 0.1 μl injected; sensitivity, 1E-9 amp/mV.

weights of the component and standard; this value could also be used as a response factor, except that in this case it would be divided into the area counts (a divisor). As defined by Equation 1, a response factor greater than 1.0 means that the detector is less sensitive to the component than to the reference material and thus the observed area must be multiplied by a number greater than 1.0 to give the same corrected area per unit weight for the component and the reference compound.

The relative weight response factor defined by Equation 1 can be transformed to the relative molar response factor by:

$$F(R\text{-molar}) = F(R\text{-weight}) \times \frac{\text{MW of ref.}}{\text{MW of comp.}} \quad \text{Eq. 2}$$

The ECN is calculated by:

$$\text{ECN-comp.} = \text{ECN-ref.} / F(R\text{-molar}) \quad \text{Eq. 3}$$

or

$$\text{ECN-comp.} = \frac{\text{MW of comp.} \times \text{ECN-ref.}}{\text{MW of ref.} \times F(R\text{-wt})} \quad \text{Eq. 4}$$

This is a generalized form of the equation given in Reference 1. Equations 3 and 4 assume a response factor of 1.0 for the reference compound. If a factor other than 1.0 is used, both equations must be multiplied by the factor used for the reference compound.

One of the reasons that the ECN calculation is not routinely used may be due to the fact that Equations 3 and 4 are not generally included in texts on the quantitative evaluation of GC data. Similarly, Equation 2 could not be found in several reference texts checked.

Equation 4 can be rewritten in a transposed form to permit calculation of relative response factors for compounds whose ECN is known or can be calculated from the contributions of the various groups in the molecule (*vide infra*):

$$F(R\text{-wt}) = \frac{\text{MW of comp.} \times \text{ECN-ref.}}{\text{MW of ref.} \times \text{ECN-comp.}} \quad \text{Eq. 4A}$$

In this form the equation is similar to that given by Kaiser (10)

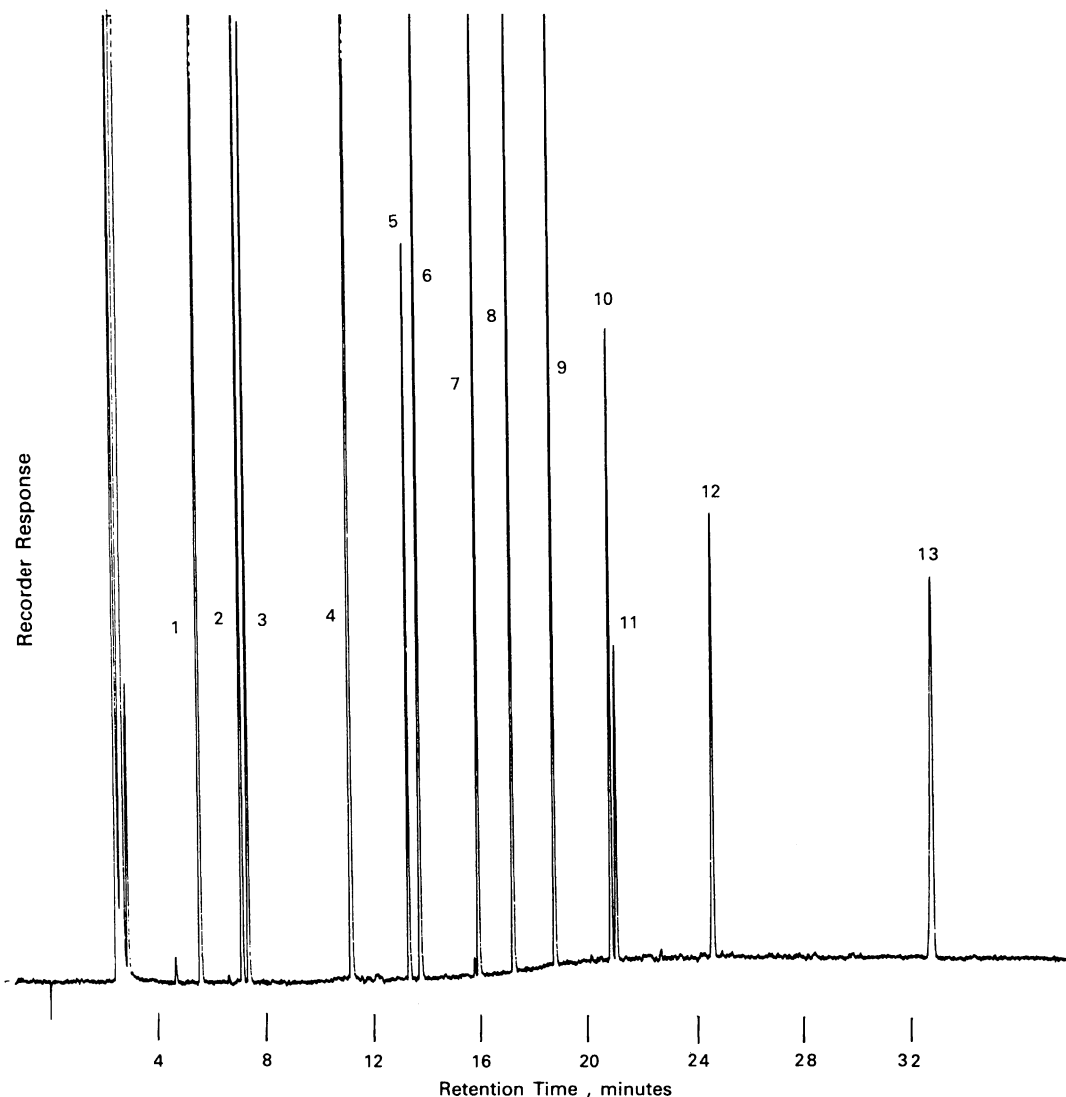


Figure 2. Chromatogram of polynuclear aromatic hydrocarbons on a chiral column. Peak identification: 1=tridecane; 2=tetradecane; 3=naphthalene; 4=2,6-dimethylnaphthalene+biphenyl; 5=acenaphthene; 6=bibenzyl; 7=fluorene; 8=diphenylacetylene; 9=*trans*-stilbene; 10=phenanthrene; 11=anthracene; 12=1-methylphenanthrene; 13=fluoranthene. Chromatographic conditions: temperature program at 70°C increased at 6°/min to 180°; 0.1 μ l injected, split ratio 50:1; sensitivity, 1E-11 amp/mV.

based on the C-factor correction proposed by Ongkeihong (11). Both equations result in the same response factors or substance-specific correction factors (10) for hydrocarbons. However, the substance-specific correction factors for oxygenated compounds (alcohols, esters, ketones) given by Kaiser do not take into account the fact that oxygen-substituted carbons produce a diminished response relative to an alkane carbon, and the ECN for the oxygenates is less than the carbon number of the molecule.

The reference material should be a hydrocarbon (n-paraffin) for which the ECN is simply the carbon number of the hydrocarbon. Sternberg et al. (1) used heptane, octane, and benzene as reference materials. Any material may be used as reference if its ECN has been determined relative to a hydrocarbon or is known from the literature. In this regard it is generally agreed that the carbonyl group in ketones and aldehydes does not contribute to the ECN (*vide infra*) and the ECN for the carbonyls is one less than the carbon number.

There is general agreement on the contribution of different functional groups to the ECN of a compound (1,2,6); these are given in Table IA. The calculated ECN is the sum of the contributions made by the various atoms comprising the molecule with corrections made for the presence of functional groups. For example, n-hexanol would have an ECN of 5.4, having six aliphatic carbons (6×1) and one primary alcohol oxygen (-0.6). A single halogen on a carbon has a negligible effect on the relative molar response, but multiple halogen substitution leads to a diminished response of about 0.12 units/halogen. The response for carbon tetrachloride is about half that of methane (1).

When used to calculate the response factor for a derivatized sample, the weight of the component in Equation 1 is the neat weight of that component, not the equivalent weight of the derivatized product. Similarly, the molecular weight of the component in Equation 4 is the molecular weight of the underivatized component. If Equation 4A is used to calculate the response factor from the theoretical ECN, then the ECN of the derivatized form is used.

The response data of Dietz (12) are given in terms of the ECN in Table II. The FID response factors in this reference are di-

vided into the area, so the reciprocal of the factors must be used in Equation 4. The calculated ECNs are in reasonable agreement with the theoretical values, assuming that the carbonyl and carboxyl groups have ECNs of zero and the ECN of alcohols is the carbon number minus approximately 0.5 (7). The calculated response factor is the value required for the ECN given in the last column, calculated from the contributions given above. Except for the esters, there are no significant differences between the reported values and the calculated factors. The response factors for the esters are based on the conclusions of Reference 2, in which it was found that the ECNs of esters were one less than the carbon number.

The following are several examples in which the use of the ECN has proved its value in analytical method development in support of projects within the authors' department.

- In selecting a column for the analysis of samples containing maleic anhydride, several glass and fused silica columns gave qualitative evidence that adequate resolution of the anhydride could be achieved with a variety of stationary phases with excellent peak shape and negligible peak tailing. However, when the ECN for maleic was calculated for each of the columns, values considerably less than the theoretical value of 2.0 were found for several of the stationary phases, including some polar silicones. With an AT-1000 fused silica column, a DEGS stainless steel SCOT column, or a glass OV-1 column, experimental ECN values of 2.0 were found.
- In the analysis of the products from the catalytic oxidation of propylene to acrolein, the porous polymer columns (e.g., Porapak Q or R) were being used to resolve the by-products

Table II. Effective Carbon Numbers from Published Response Data (12) Calculated Relative to Heptane

Compound	Factor (reference)	ECN	Factor (calculated)	ECN (theory)
Acetylene	1.07	1.95	1.10	2
Ethylene	1.02	2.00	1.02	2
Hexene	0.99	5.82	1.02	6
Methanol	0.23	0.52	0.222	0.5
Ethanol	0.46	1.48	0.466	1.5
n-Propanol	0.60	2.52	0.595	2.5
i-Propanol	0.53	2.24	0.595(0.54)	2.5(2.25)
n-Butanol	0.66	3.42	0.676	3.5
Amyl alcohol	0.71	4.37	0.731	4.5
Butanal	0.62	3.12	0.596	3
Heptanal	0.77	6.14	0.752	6
Octanal	0.78	6.99	0.782	7
Capric aldehyde	0.80	8.73	0.824	9
Acetic acid	0.24	1.01	0.238	1
Propionic acid	0.40	2.07	0.386	2
Butyric acid	0.48	2.95	0.487	3
Hexanoic acid	0.63	5.11	0.616	5
Heptanoic acid	0.61	5.55	0.660	6
Octanoic acid	0.65	6.55	0.695	7
Methyl acetate	0.20	1.04	0.386	2.0*
Ethyl acetate	0.38	2.33	0.487	3.0*
i-Propyl acetate	0.49	3.52	0.561	4.0*
n-Butyl acetate	0.55	4.46	0.616	5.0*
Acetone	0.49	2.00	0.49	2
Methyl ethyl ketone	0.61	3.07	0.596	3
Methyl i-butyl ketone	0.71	4.97	0.716	5
Ethyl butyl ketone	0.71	5.66	0.752	6
Di-i-butyl ketone	0.72	7.15	0.805	8
Ethyl amyl ketone	0.80	7.16	0.782	7
Cyclohexanone	0.72	4.94	0.729	5

*From Reference 2: ECN of ester = carbon number - 1

Table I. Contributions to the Effective Carbon Number

Atom	Derivatized form	Type	ECN contribution
<i>A. As determined by Sternberg et al. (1)</i>			
C		Aliphatic	1
C		Aromatic	1
C		Olefinic	0.95
C		Acetylenic	1.30
C		Carbonyl	0
C		Carboxyl	0
C		Nitrile	0.3
O		Ether	-1.0
O		Primary alcohol	-0.5
O		Secondary alcohol	-0.75
O		Tertiary alcohol	-0.25
N		Amine	As O in alcohols
Cl		2+-Aliphatic	-0.12 per chlorine
Cl		On olefinic C	+0.05
<i>B. As determined in this study for derivatized compounds</i>			
	H-C-O-TMS (alcohol)		3.69-3.78
	CO ₂ -TMS (acid)		3.0
	CH=N-O-TMS (silyl oxime)		3.3
	CH=N-O-CH ₃ (methoxime)		0.92-1.04

acetic and acrylic acids. Qualitatively, the acids were well resolved as reasonably symmetrical peaks from the other products in the samples. The FID was required to provide the sensitivity needed for the low levels of the oxygenated by-products. Although acetic acid gave the expected ECN of 1.0, acrylic acid gave an ECN of approximately 1.5 (expected 2.0) and lower. The ECN for acrylic acid was approximately the same for columns prepared from stainless steel, nickel, and glass. Analysis of the standards on either a fused silica AT-1000 capillary column or a Series 530 μ Carbowax 20M column (Hewlett-Packard) gave the expected ECN of 2.0. The problem with apparent adsorption or reaction of acrylic acid on the porous polymers did not appear to be present with the other oxygenated materials in the samples (e.g., acetaldehyde, acrolein, allyl alcohol), as the ECNs for the compounds were as predicted by theory and did not change with the component levels in the standards. Propionic acid gave the expected ECN of 2.0 on the porous polymer columns. Studies are continuing to determine if this unexpected result is also present with other porous polymer columns.

Table III. Relative Response Factors and Effective Carbon Numbers for Trimethylsilylated Alcohols, Polyols, and n-Acids With Tetradecane as Reference

Component	Factor	RSD	ECN	F(R)-calculated
Heptanol	0.825	0.30	9.94	0.846*
Octanol	0.878	0.26	10.47	0.859*
Decanol	0.871	0.20	12.82	0.880*
Dodecanol	0.923	0.54	14.25	0.895*
1-Phenyl ethanol	0.797	0.50	10.82	0.806*
2-Phenyl ethanol	0.802	0.40	10.75	0.806*
Ethylene glycol	0.579	0.41	7.56	0.594*
Glycerol	0.596	0.40	10.91	0.587*
Erythritol	0.579	0.54	14.89	0.588*
Xylitol	0.577	0.60	18.62	0.582*
Sorbitol	0.598	0.83	21.48	0.581*
Diethylene glycol	0.927	0.34	8.07	0.893**
Triethylene glycol	1.160	0.46	9.13	1.130**
Tetraethylene glycol	1.346	0.46	10.18	1.319**
Hexanoic acid	1.025	0.45	8.00	1.025***
Heptanoic acid	1.043	0.15	8.80	1.021***
Octanoic acid	1.024	0.08	9.94	1.018***
Nonanoic acid	1.031	0.24	10.83	1.015***

*Assuming ECN of H-C-O-TMS = 3.69 and 1.0 for remaining carbons.

**Assuming ECN of H-C-O-TMS = 3.69 and -C-H₂O-CH₂- = 1.0

***Assuming ECN of -C-O₂-TMS = 3.0 and 1.0 for remaining carbons.

• It is not always possible or desirable to analyze functional or polyfunctional organic compounds in the neat form. Many of the mixtures for which analyses are required must be derivatized in some manner before GC analysis. The polyols and carbohydrates are examples of compounds which necessitate derivatization. The polyols can be easily analyzed as the TMS-derivatives and the carbohydrates are quantitatively converted to the TMS-oxime derivatives by a procedure previously described (9). It was previously found that the TMS-polyols and the TMS-oxime-carbohydrates had, within experimental error, the same relative response factors (9). Similar mixtures have been re-analyzed and the response factors and ECNs determined relative to a hydrocarbon (Tables III and IV). The ECNs are calculated using the molecular weight of the parent compound in Equation 4, not the molecular weight of the derivatized product.

The polyols give an average ECN of 3.69 per H-C-O-TMS group with a relative standard deviation of 2.1% for trimethylsilylated ethyleneglycol through sorbitol. The calculated response factors for this average (last column in Table III) are in reasonable agreement with the experimentally determined values.

Although there is a greater scatter in the calculated ECNs for the linear alcohols, the calculated relative response factors, assuming the contribution from the H-C-O-TMS is 3.69 and a contribution of 1.0 for the remaining carbons, are not significantly different from the experimental values.

Within the limits of experimental error, there was no difference in the relative response factors and ECNs for 1- and 2-phenyl ethanol. The average ECN was 10.78, corresponding to an ECN contribution of 3.78 for the C-O-TMS group. This value is only 2.5% higher than those found for the alcohols and polyols. Further studies are needed to determine if the derivatized forms of primary, secondary, and tertiary alcohols exhibit differences in response as has been reported for the neat alcohols (1,2,6).

With the exception of ethylene glycol, the ECNs for the polyethylene glycols (di- through tetra-) appear to increase by one unit, consistent with an ECN of 1.0 for -CH₂-O-CH₂- (6). The response factors for this oligomeric series increase much more rapidly than is observed for homologs.

The ECNs of the derivatized carbohydrates are composed of the contribution made by the H-C-O-TMS groups and the CH=N-O-TMS or CH=N-O-CH₃ group in the derivatized samples. Both acetophenone and benzophenone give an ECN of

Table IV. Relative Response Factors and Effective Carbon Numbers for Carbohydrates and Aromatic Carbonyls as TMS-Oximes and TMS-Methoximes With Tetradecane as Reference

Component	Experimental				Calculated			
	TMS-oximes		TMS-methoximes		TMS-oximes		TMS-methoximes	
	Factor	ECN	Factor	ECN	Factor	ECN	Factor	ECN
Acetophenone	0.823	10.3	1.054	8.04	0.823	10.3	1.054	8.04
Benzophenone	0.839	15.33	0.996	12.92	0.840	15.3	0.986	13.04
Dihydroxyacetone	0.598	10.69	0.780	8.15	0.595	10.68	0.755	8.42
Glyceraldehyde	0.601	10.58	0.776	8.20	0.595	10.69	0.755	8.42
Erythrose	(not available)	(not available)	(not available)	(not available)	0.590	14.37	0.700	12.1
Ribose	0.583	18.18	0.662	16.00	0.587	18.06	0.671	15.8
Xylose	0.592	17.90	0.671	15.8	0.587	18.06	0.671	15.8
2-Deoxy-galactose	0.599	19.4	0.710	16.3	0.608	19.1	0.690	16.8
Galactose	0.573	22.2	0.664	19.2	0.584	21.75	0.652	19.49
Fructose	0.586	21.7	0.664	19.2	0.584	21.75	0.652	19.49

3.3 for the $\text{CH}=\text{N}-\text{O}-\text{TMS}$ group. The ECN for the $\text{CH}=\text{N}-\text{O}-\text{CH}_3$ group is 1.04 for acetophenone and 0.92 for benzophenone. Using the values of 3.3 for the TMS-oxime group, 1.04 for the methoxime group, and assuming that the contribution of the $\text{H}-\text{C}-\text{O}-\text{TMS}$ group is the same as in the polyols, the ECNs and relative response factors were calculated for these compounds (Table IV, right-hand columns). The calculated values are in essential agreement with the experimentally determined values for those components which could be obtained in sufficient purity for determination of the relative response factors. The tetroses (e.g., threose and erythrose) are not commercially available for comparison, hence the calculated response factor would have to be used.

Benzophenone was analyzed neat and as the methoxime, ethoxime, and TMS-oxime derivatives. An ECN of 12.0 was found for the neat material (Table V). The ECNs for the TMS-oxime, methoxime, and ethoxime were 15.3, 12.92 (Table IV), and 13.63, respectively. These data suggest that the aromatic carbons make an ECN contribution of 1.0 (as expected), the $=\text{C}=\text{N}-\text{O}$ group has an ECN of 0.3, and the $\text{O}-\text{CH}_3$ group has an ECN of 0.6. The ECN of the $\text{O}-\text{CH}_2-\text{CH}_3$ group in the ethoxime derivative on this basis would only be 1.3, slightly lower than expected if the ECN of the methoxy group was 0.6. If the ECN of the ethoxime derivative was 13.9, the relative response factor would have been 0.923 as compared to the experimentally determined value of 0.943, an error of about 2%.

Another class of compounds which are amenable to analysis after trimethylsilylation are the mono- and di-carboxylic acids. Results with a limited number of mono-carboxylic acids (Table III) indicate that the TMS-carboxy group has an ECN of 3.0 consistent with a zero contribution for the carboxy group and a unit contribution for each methyl group in TMS.

The results for the ECN contributions from the TMS-alcohols and TMS-acids can be combined to calculate response factors for hydroxy acids which are not commercially available. Although some of the hydroxy acids (e.g., glycolic and lactic) are commercially available in pure crystalline form, others such as glyceric or threonic acids cannot be obtained in pure form. As the TMS-derivatives, the ECN is the sum of the contributions made by the alkane portion, the $\text{H}-\text{C}-\text{O}-\text{TMS}$ portions, and the CO_2-TMS portions of the derivatized form. This results in an ECN of 6.69 for glycolic acid, 7.69 for lactic acid, 10.38 for glyceric acid, and 14.07 for threonic acid. The relative response factors for these acids can then be calculated relative

to any chosen reference material.

• The analysis of polycyclic aromatic hydrocarbons (PAH) is an interesting test of the ECN concept. Some response data have been published (13-15), but not in all cases calculated relative to an alkane (13). The recent data of Tong and Karasek (14) indicate that the PAHs yield lower counts per unit weight than the paraffinic hydrocarbons. In terms of a relative response factor, this means that the observed areas for the PAHs must be multiplied by a factor >1.0 to give equal corrected areas per unit weight. According to their data (Reference 14, Table V) the PAHs have response factors of 1.08 relative to the alkanes. The ECNs calculated from their data are 1.5 to approximately 3.5 units lower than the actual carbon numbers of the PAHs when calculated relative to tetradecane as a reference. The PAHs, having a higher carbon content than the paraffins, should have response factors <1.0 relative to the alkanes on an equal response per unit weight of carbon. This was what was found for a small, but somewhat representative group of PAHs, as shown in Table V. Under the conditions given in the Experimental section, all of the compounds gave response factors relative to tridecane or tetradecane <1.0 and the ECNs are in exact or substantial agreement with that predicted by Equation 4. In those cases where the calculated ECN is significantly different (5% or greater) from the expected value, there is some question relative to the purity of the chemical used. Excluding the value for diphenylacetylene, the average percent accountability of the ECN for the remaining eleven PAHs is 98.4% with a relative standard deviation of 2.3%. The relative response factors and ECNs were the same on this column at 1:5 and 1:10 dilutions of the standard solutions.

The response factors for the PAHs were increased by an average of about 3% (relative) when the amount on column was reduced by a factor of 50 with split injection (Table VI). The factors were increased slightly more when the amount on column was further reduced to about 1 ng/component. This increase may have been due to adsorption by the column or by biasing in the split ratio for this wide boiling range of materials at high dilution. Even at the lower level, the response factors were still <1.0 .

The use of flash-vaporization for the analysis of the high-boiling PAHs may lead to more serious errors in quantitation than cold on-column injection. An injection port temperature of 300° to 320°C was required to achieve reproducible results in the analysis of standards containing fluoranthene (b.p. 393°C). Whatever technique is used, the data presented con-

Table V. Relative Response Factors and Effective Carbon Numbers for Aromatic Hydrocarbons*

Component (carbon number)	Factor	RSD (%)	ECN	% ECN**
Biphenyl (12)	0.922	0.33	11.79	98.3
Bibenzyl (14)	0.911	0.75	14.11	102.1
Diphenylacetylene (14)	0.984	0.85	12.77	91.2
<i>trans</i> -Stilbene (14)	0.916	1.2	13.87	99.1
Naphthalene (10)	0.903	0.61	10.01	100.1
Dimethylnaphthalene (12)	0.922	0.39	11.95	99.6
Acenaphthene (12)	0.905	0.91	12.01	100.1
Fluorene (13)	0.922	0.30	12.73	97.9
Phenanthrene (14)	0.935	0.36	13.46	96.1
Methylphenanthrene (15)	0.957	1.7	14.17	94.5
Fluoranthene (16)	0.926	0.66	15.41	96.3
Benzophenone (13)	1.074	0.80	11.98	—

*A Series 530 μ column with 50-500 ng/component on-column was used.

**% ECN = calculated ECN $\times$ 100/carbon number

Table VI. Relative Response Factors and Effective Carbon Numbers for Aromatic Hydrocarbons*

Component	Amount used on column			
	10 ng/component		1 ng/component	
	F(R)	RSD(%)	F(R)	RSD(%)
Naphthalene	0.921	1.29	0.936	1.94
Dimethylnaphthalene	0.937	1.20	0.951	1.25
Acenaphthene	0.933	1.23	0.952	1.36
Fluorene	0.963	1.32	0.985	1.94
Phenanthrene	0.981	1.35	0.996	1.94
Methylphenanthrene	0.988	1.39	0.990	1.63
Fluoranthene	0.960	1.38	0.960	1.56

*A chiral column with split injection was used.

firm the fact that the FID functions on an equal response per unit weight of carbon and the response factors for the higher PAHs should reflect this performance. Response factors significantly greater (or conversely, ECNs significantly lower) than predicted by the chemical structure may be due to less-than-adequate column deactivation and incomplete elution of the PAHs (16). Experimentally determined response factors are also inversely related to the purity of the compound being tested. It should be noted that it was not the original intent of this paper to investigate the relative response data for the PAHs. Hence the study has dealt with only a few selected (available) compounds and the relationship of their response data in terms of the ECNs.

- It is not always possible to secure a compound of sufficient purity to determine its relative response factor. In many cases the factor is set equal to a similar compound in the mixture or simply set equal to 1.0. If the ECN of the component in either its neat or derivatized form can be calculated from the sum of the ECNs of the groups comprising the molecule, Equation 4A can be used to calculate the relative response factors. Using this equation, the response factors for a series of ethylene oxide (EO) adducts of dodecanol as the TMS and acetate derivatives have been calculated. Although adducts having a narrow range of EOs are available, individual components were not available for the determination of the relative response factors.

For the TMS derivatives of the adducts, the value of 3.69 was used for the contribution of the $\text{CH}_2\text{-O-TMS}$ group and each EO was assumed to contribute one unit to the ECN, giving the equation:

$$F(R) = \frac{(186 + 44n) \times 14.69}{(14.69 + n) \times 186} \quad \text{Eq. 5}$$

where 186 is the molecular weight of dodecanol (used as reference) and $186 + 44n$ is the molecular weight of the adduct containing n EO units. The response factors are shown in Table VII. The ECN of dodecyl acetate was assumed to be 12.5 and that of the adducts $12.5 + n$. Using these values in Equation 5 gives the factors shown in Table VII.

The response factors for either the TMS or acetate derivatives do not increase in a linear fashion, but rather show the greatest relative differences at low values of n . The response factors increase by 0.04 to 0.07 units at higher values of n . McClure (17) used an average difference of 0.04 between $n = 3$

and 8. Studies are in progress to test the validity of these calculated response factors and will be reported separately.

Conclusions

The calculation of the effective carbon number is an easy means for verifying the accuracy of experimentally determined relative response factors using the flame ionization detector. Not only can it be used for the evaluation of data for components analyzed in the neat form, but can also be used for components which have been chemically derivatized, e.g., silylated. When the derivatized form increases the number of FID-active groups, the calculated ECN can be correlated to the structure of the derivatized form.

To the list of contributions to the ECN shown in Table IA can be added the values derived in this study for derivatized functional organic compounds, as given in Table IB.

The calculation will probably not be accurate for the analysis of compounds containing electron-absorbing groups (e.g., halogens), as the signal will be decreased by the competing electron-capture process. Anomalous results have been found in the analysis of perfluorinated acids and alkanes (18,19). Further work needs to be done to quantify the effect of other groups.

With the many improvements which have been made in column technology, detector design, and data handling systems, the use of the effective carbon number concept deserves continued investigation to more fully understand the relationships between molecular structure and the response of the flame ionization detector.

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Table VII. ECN-Calculated Relative Response Factors for EO Adducts of Dodecanol

n	F(R)—weight basis vs. dodecanol	
	TMS-derivatives	Acetate derivatives
0	1.00	1.00
1	1.16	1.14
2	1.30	1.27
3	1.42	1.38
4	1.53	1.47
5	1.63	1.56
6	1.72	1.63
7	1.80	1.70
8	1.87	1.76
9	1.94	1.82
10	2.00	1.87

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