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Investigation of General Expression to Predict the Molar Response Factor in the GC for Monosubstituted Alkanes

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Abstract

The flame ionization detection relative molar response factors (f_M) are determined by experiments for 23 monosubstituted alkanes RX (X = Cl, OH, SH, and NH_2). A new molecular descriptor, modified inner molecular polarizability index ($IMPI_m$), is developed. Using the $IMPI_m$, the number of hydrogen atoms (N_H) on the group X and the group electronegative X_p as variables, the obtained f_M values as functions, a general expression to predict molar response factor values, is established. The credibility of the expression is confirmed by both of the leave-one-out method and the detection of model mixture.

Introduction

Flame ionization detection (FID) is the most commonly used detector for gas chromatography (GC) due to its high sensitivity for organic compounds. In general, the FID response factors of homologous compounds are proportional to their number of carbon atoms or molar mass (1–3). However, this rule is no longer followed when considering a different series of organic compounds. That is, the FID responses depend heavily on the molecular structures and characteristic. To obtain more acceptable quantitative analytical results, it is necessary to predict the chromatographic factors by using the method of quantitative structure-property relationship (QSPR). In other words, the quantitative relationship between the quantity and the peak area of an analyte is the key information for quantitating the analyte with a GC method. Jalavi-Heravi et al. (4–8) used the artificial neural networks to predict FID, thermal conductivity detection (TCD), and photoionization detection (PID) response factors. But the parameters of this method are many and hard to obtain. Then, the multiple linear regression method was the most popular method used (9–12). The first work on the prediction of response factors of substituted benzenes and pyndines was published by Katrizky and Gordeeva (9). With the aid of a computer, Stanton and Jurs (10,11) even used multiple linear regressions to generate model equations of relating structural features to observed retention characteristics. Also, Katrizky et al. (12) applied the multiple linear regression methods to predict the retention time and response factors for 152 individual structures and obtained good correlations with six-parameter for gas chromatographic retention times ($R_{cv}^2 = 0.955$) and for response factors ($R_{cv}^2 = 0.811$).

In this paper, the FID molar response factors were determined for the monosubstituted alkanes RX (X = Cl, OH, SH, and NH_2). Furthermore, a new molecular structure descriptor, modified inner molecular polarizability index ($IMPI_m$), was proposed. Take the $IMPI_m$ together with the group electronegative (X_p) and the number of H on the group X (N_H) as parameters, the correlation between the molar response factors and the three parameters was investigated for the mentioned compounds.

Experimental

Instrumentation

The GC used was an Autosystem XL (Perkin-Elmer, Waltham, MA). The packed column used was a 15% DNP. The chromatographic conditions were as follows: pure nitrogen was used as a carrier gas at a flow rate of 20 mL/min, the injector temperature was maintained at 160°C, the oven temperature was maintained at 125°C, and the FID temperature was maintained at 200°C.

Reagents and chemicals

Chemicals were analytical-reagent grade and were purchased from J&K Chemical (Beijing, China). The liquid reagents and solvents used in the experiments were distilled, and their purities were confirmed by GC. The analytes are listed in Table I.

Experimental work

Hexane was chosen as the internal standard. For each analyte, i, an amount of analyte, n_i (0.01–0.05 mol), was mixed with a known amount of hexane, n_{c6} (0.01–0.05 mol), at below 20°C, and, thus, five samples of different molar ratio, M_{rel} of the analyte, i, to hexane (where $M_{rel} = n_i/n_{c6}$) were prepared. Then each resulting blend was detected two times separately, in which the volume or mass of the blends injected need not to be known, because its molar ratio of the analyte to hexane was known.

For each sample of M_{rel}, two peak areas from separate experiments were selected and its mean peak area was calculated for analyte i and for hexane. Here the mean peak area of analyte i is

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expressed by the symbol, A_i, and that of hexane by the symbol A_{C6}. Thus, the relative peak area A_{rel} of analyte *i* to hexane was calculated by equation 1.

$$A_{rel} = A_i/A_{C6} \qquad \text{Eq. 1}$$

Then the correlation between the relative mean peak area and the molar ration was carried out for each given analyte.

Calculation of the molar response factor

Based on the principle of GC quantitative analysis, for a given analyte, its quantity (Q) and peak area (A) can be expressed (13) with equation 2.

$$Q = f'A \qquad \text{Eq. 2}$$

Where f' is the coefficient, named as the quantitative response factors. Often it is another form, relative molar response factor, f_M, that is used. That is:

$$f_M = \frac{f'_{M(i)}}{f'_{M(s)}} = \frac{m_iA_sM_s}{m_sA_iM_i} = \frac{[m_i/M_i]/[m_s/M_s]}{A_i/A_s} = \frac{M_{rel}}{A_{rel}} \qquad \text{Eq. 3A}$$

or

$$M_{rel} = f_MA_{rel} \qquad \text{Eq. 3B}$$

Here i and s denote analyte and standard compound, respectively; m is mass; M is molar mass; M_{rel} is molar ratio n_i/n_s. In this paper, the f_M values of monosubstituted alkanes RX were calculated from the obtained relative peak area A_{rel} with equation 3 and were related to its molecular structure.

Take 2-methy-propanol for an example, its experimental relative peak area and molar ratio are listed in Table II. When M_{rel} is related to A_{rel}, the regression equation (equation 4) was obtained.

$$M_{rel} = 1.5862\ A_{rel} \qquad \text{Eq. 4}$$

Where $R = 0.9991$, $S = 0.0631$, $F = 2227.1740$, and $n = 5$.

Equation 4 shows that the f_M of 2-methy-propanol is 1.5862. With the previous calculating method, the f_M values of all 23 monosubstituted alkanes RX were obtained (see Table III). The data of experimental relative peak area (A_{rel}) and molar ratio of compounds RX can be seen from the appendix.

Calculation of molecular structure descriptor

Modified inner molecular polarizability index ($IMPI_m$)

In our recent work (14), the parameter inner molecular polarizability index (IMPI) was proposed to describe the molecular structure of alkane, which was calculated by equation 5.

$$IMPI = \Sigma PEI(i) \qquad \text{Eq. 5}$$

Where PEI(i) is the sum of the polarizability effect index of alkyl groups connected to the ith carbon atom. In other words, equation 5 also can be expressed as follows:

$$IMPI = \Sigma[RE \times PE] \qquad \text{Eq. 6}$$

where RE is the relative electronegativity matrix, $RE = [X_{rel,1}, X_{rel,2}, \ldots X_{rel,n}]$, and the element $X_{rel,i} = X_i/2.55$ (X_i and 2.55 are the Pauling electronegativities of the ith vertex and carbon atom, respectively). For alkanes, all $X_{re,i}$ are equal to 1; PE is the polarizability effect matrix, that is $PE = [\Delta PEI_{ij}]$. The values of ΔPEI_{ij} were constructed as follows: when vertex i = j, let $\Delta PEI_{ij} = 0$; when $i \neq j$ and the distance between i and j is l (the number of chemical bond), the $\Delta PEI_{ij} = \Delta PEI(l)$. The value of $\Delta PEI(l)$ is the polarizability effect index increment and can be directly taken from Table I of our previous work (15).

Take *n*-butane as an example, its hydrogen suppressed graph is shown in Figure 1.

RE = [1,1,1,1]

$$PE_{n\text{-propanol}} = \begin{bmatrix} 0 & 1 & 0.1405 & 0.0481 \\ 1 & 0 & 1 & 0.1405 \\ 0.1405 & 1 & 0 & 1 \\ 0.0481 & 0.1405 & 1 & 0 \end{bmatrix}$$

$IMPI_{n\text{-butane}} = \Sigma\ [RE \times RE] = \Sigma\ [1.1886, 2.1405, 2.1405, 1.1886] = 6.6582$.

However, compared with the alkane, the monosubstituted alkane RX has polarity, and its

Table I. The Molar Mass and Boiling Point for Analytes

No.	Compound	Molar mass	Bp(°C)*	No.	Compound	Molar mass	Bp(°C)*
1	Butanol	74.12	116	13	Chloropentane	106.59	107
2	2-Methy-propanol	74.12	83	14	2-Chloropentane	106.59	96.9
3	2-Butanol	74.12	99.5	15	3-Methy-chlorobutane	106.59	98.9
4	3-Methy-butanol	88.14	112	16	Chlorohexane	120.62	135
5	2-Methy-2-butanol	88.14	102	17	Cyclochlorohexane	118.60	142
6	2-Pentanol	88.14	118	18	Chlorooctane	148.67	183
7	3-Pentanol	88.14	115	19	Amylamine	87.16	104
8	Hexanol	102.17	156	20	3-Methylbutylamine	87.16	95-97
9	Cyclohexanol	100.16	161	21	Hexylamine	101.19	130
10	Heptanol	116.20	176	22	Hexanethiol	118.23	150–154
11	Octanol	130.23	195	23	3-Methylbutanethiol	104.21	120
12	Chlorobutane	92.56	78	24	Hexane	86.18	68.5–69.5

* Boiling point.

Table II. Experimental Relative Peak Area and Molar Ratio for 2-Methy-Propanol

	First			Second			Mean of
M_{rel}	A_{hexane}	$A_{2\text{-methy-propanol}}$	A_{rel}	A_{hexane}	$A_{2\text{-methy-propanol}}$	A_{rel}	A_{rel}
0.4830	4538080.74	1297310.58	0.2859	4374312.65	1194919.50	0.2732	0.2796
0.9455	4813924.40	2865804.81	0.5953	4591634.76	2661786.54	0.5797	0.5875
1.8618	1844719.28	1965519.99	1.0655	2377767.19	2718893.00	1.1435	1.1045
2.9607	1630054.45	3080446.44	1.8898	1637798.42	3096152.51	1.8904	1.8901
4.1331	2072719.24	5324643.00	2.5689	2011514.71	5382694.98	2.6759	2.6224

heteroatomic electronegativity is no longer equal to that of the carbon atom. Hence, the IMPI of RX is different from that of alkane, and it must be modified. In this work, the IMPI was modified as modified inner molecular polarizability index ($IMPI_m$). To obtain the $IMPI_m$ of RX, the electronegativity of heteroatoms is introduced into the RE matrix. The calculation of $IMPI_m$ for *n*-propanol (see Figure 2), for example, is described as follows.

$$RE_{n\text{-propanol}} = [2.55/2.55, 2.55/2.55, 2.55/2.55, 3.44/2.55] = [1, 1, 1, 1.3490]$$

$$PE_{n\text{-propanol}} = \begin{bmatrix} 0 & 1 & 0.1405 & 0.0481 \\ 1 & 0 & 1 & 0.1405 \\ 0.1405 & 1 & 0 & 1 \\ 0.0481 & 0.1405 & 1 & 0 \end{bmatrix}$$

$$IMPI_{m,n\text{-propanol}} = \Sigma[RE_{n\text{-propanol}} \times PE_{n\text{-propanol}}] = \Sigma[1.2054, 2.1895, 2.4895, 1.1886] = 7.0730$$

With the same method, the $IMPI_m$ values were calculated for 23 monosubstituted alkanes RX and are listed in Table III.

The number of hydrogen in group X and the electronegativity of group X

Here, the number of hydrogen atoms in group X (N_H) is also chosen as a molecular structure parameter. For the groups OH, SH, and NH_2, their N_H values are 1, 1, and 2, respectively, and for the halogen atom, $N_H = 0$.

In regards to the electronegativity of group X (X_P), according to Exner and Bohm's recent work (16), the electronegativity of a group X can be expressed by the electronegativity of its radical atom (for example, the electronegativity of OH group is expressed by that of O atom, 3.44). So this method also is employed in this paper.

Results and Discussion

It can be seen from Table III that: (*i*) for the same sort of compounds, their relative molar response factors vary with the change of carbon atom numbers. Even for the isomers, their relative molar response factors are also unequal. (*ii*) The differences of relative molar response factors exist among the different kinds of compounds. Roughly, for the different monosubstituted alkanes RX with the same carbon atom number, their relative molar response factors are in the order: R-OH < R-Cl < R-SH < R-NH_2.

This implies that the relative molar response factor of compound RX was affected by its molecular skeleton and the group X. Therefore, this paper takes parameters $IMPI_m$, N_H, and X_P to correlate the f_M for the compound's RX. Additionally, according to the author's recent work (17,18), the interaction between the alkyl R and the group X should be taken into account in the study of the property of RX. Therefore, the item X_pIMPI_m was employed in the regression analysis. The obtained correlation equation is shown as follow.

$$f_M = -0.2402\ IMPI_m + 0.0096(IMPI_m)^2 + 0.1271N_H - 0.0305(X_p \times IMPI_m) + 3.9557 \qquad \text{Eq. 7}$$

where $R = 0.9836$, $S = 0.0499$, $F = 134.1818$, $n = 23$, $R_{cv} = 0.9448$, and $S_{cv} = 0.0577$

To verify the reliability of equation 7, a cross validation was performed by a leave-one-out (loo) method, yielding R_{cv} =

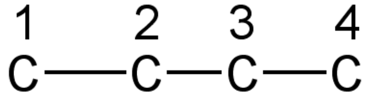

Figure 1. The hydrogen suppressed graph of *n*-butane.

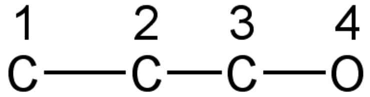

Figure 2. The hydrogen suppressed graph of *n*-propanol.

Table III. The Relative Molar Response Factor (f_M) and Molecular Structure Parameters for 23 RX Compounds

No.	Compound	$f_{M(exp.)}$*	$f_{M\ (cal.)}$†	$f_{M\ (loo.)}$‡	$IMPI_m$§	NH**	Xp††
1	Butanol	1.6761	1.6705	1.6687	9.5054	1	3.44
2	2-Methy-propanol	1.5862	1.6316	1.6430	9.748	1	3.44
3	2-Butanol	1.6716	1.6265	1.6155	9.7803	1	3.44
4	3-Methy-butanol	1.3049	1.3001	1.2995	12.2188	1	3.44
5	2-Methy-2-butanol	1.1574	1.2422	1.2542	12.7685	1	3.44
6	2-Pentanol	1.3115	1.2956	1.2936	12.2597	1	3.44
7	3-Pentanol	1.2597	1.2893	1.2929	12.3175	1	3.44
8	Hexanol	1.0837	1.1024	1.1060	14.435	1	3.44
9	Cyclohexanol	1.0456	0.9870	0.9746	17.2649	1	3.44
10	Heptanol	1.0286	0.9928	0.9857	16.9198	1	3.44
11	Octanol	0.9363	1.0020	1.0544	19.4135	1	3.44
12	Chlorobutane	1.6743	1.6452	1.6312	9.3724	0	3.16
13	Chloropentane	1.3788	1.3186	1.3077	11.8275	0	3.16
14	2-Chloropentane	1.3398	1.2884	1.2787	12.1112	0	3.16
15	3-Methy-chlorobutane	1.2294	1.2913	1.3028	12.0832	0	3.16
16	Chlorohexane	1.0625	1.1067	1.1174	14.2994	0	3.16
17	Cyclochlorohexane	1.0409	1.0082	1.0005	17.1111	0	3.16
18	Chlorooctane	1.0392	1.0358	1.0331	19.2767	0	3.16
19	Amylamine	1.6541	1.6221	1.6134	11.7698	2	3.04
20	3-Methylbutylamine	1.5976	1.5955	1.5949	12.025	2	3.04
21	Hexylamine	1.4531	1.4165	1.4046	14.2413	2	3.04
22	Hexanethiol	1.5167	1.4997	1.4890	14.0185	1	2.58
23	3-Methylbutanethiol	1.5770	1.6571	1.6887	11.8021	1	2.58

* Experimental values.
† Calculation values from equation 7.
‡ Predicted values by the leave-one-out.
§ Modified inner polarizability index.
** The number of H on the group X.
†† Electronegative of group X.

Table IV. The M_{rel} and the $M_{rel, exp}$ for Chloroheptane and Propanol in Model Mixture

	First		Second			
Compound	A_{rel}	M_{rel}	A_{rel}	M_{rel}	Average M_{rel}	$M_{rel, exp}$
Chloroheptane	1.4229	1.4358	1.3803	1.3929	1.4144	1.4495
Propanol	1.0049	2.1324	0.9775	2.0743	2.1034	2.1674

0.9448, S_{cv} = 0.0577. The calculated values $f_{M(cal.)}$ with equation 7 and the predicted values $f_{M\ (loo)}$ by the loo method are listed in Table III (see the 4th and 5th column).

Further, a model mixture of compounds, including chloroheptane, propanol, and hexane was employed, and its components were determined. As the relative molar response factors of chloroheptane and propanol were not measured, they must be predicted with equation 7. For chloroheptane and propanol, the $IMPI_m$ were 16.9198 and 7.0730, and the group electronegativities of Cl and OH were 3.16 and 3.44, respectively. Thus their f_M values can be calculated as follows.

$$f_{M(chloroheptne)} = -0.2402 \times 16.9198 + 0.0096 \times (16.9198)^2 + 0.1271 \times 0 - 0.0305 \times (3.16 \times 16.9198) + 3.9557 = 1.0091$$

$$f_{M(propanol)} = -0.2402 \times 7.0730 + 0.0096 \times (7.0730)^2 + 0.1271 \times 1 - 0.0305 \times (3.44 \times 7.0730) + 3.9557 = 2.1220$$

With the observed peak area and the described predicted relative molar response factors, the molar ratio of chloroheptane–propanol to hexane M_{rel} (see Table IV) can be calculated by equation 3B. The calculated M_{rel} was in good agreement with the actual values of the experimental values $M_{rel, exp}$ (see Table IV, the $M_{rel, exp}$). The results of Table IV confirmed that equation 7 was credible.

Conclusion

From the previously described results, it can be seen that it is possible to estimate the molar response factor of monosubstituted alkanes RX with a general expression. The present method has the notable merit of structure parameters derived easily from the molecular structures. This work explores a novel way to investigate the correlation between the molecular structure and molar response factor for monosubstituted alkanes.

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Appendix

Table I. Experimental Relative Peak Area and Molar Ratio for Butanol

	First			Second			
M_{rel}	A_{hexane}	$A_{butanol}$	A_{rel}	A_{hexane}	$A_{butanol}$	A_{rel}	Mean A_{rel}
0.5707	3021040.89	116241.97	0.0385	2862760.22	109402.03	0.0382	0.0384
0.9989	2961228.13	1406702.31	0.4750	3315539.66	1666474.23	0.5026	0.4888
1.9678	2323395.57	2499767.01	1.0759	2531321.25	2587921.67	1.0224	1.0492
2.8067	1966945.01	3102202.35	1.5772	1829048.12	2927376.2	1.6005	1.5889
3.4791	1540167.12	3470299.48	2.2532	1834513.42	4028200.89	2.1958	2.2245

Table II. Experimental Relative Peak Area and Molar Ratio for 2-Methy-Propanol

	First			Second			
M_{rel}	A_{hexane}	$A_{2\text{-methy-propanol}}$	A_{rel}	A_{hexane}	$A_{2\text{-methy-propanol}}$	A_{rel}	Mean A_{rel}
0.4830	4538080.74	1297310.58	0.2859	4374312.65	1194919.5	0.2732	0.2796
0.9455	4813924.4	2865804.81	0.5953	4591634.76	2661786.54	0.5797	0.5875
1.8618	1844719.28	1965519.99	1.0655	2377767.19	2718893.00	1.1435	1.1045
2.9607	1630054.45	3080446.44	1.8898	1637798.42	3096152.51	1.8904	1.8901
4.1331	2072719.24	5324643.00	2.5689	2011514.71	5382694.98	2.6759	2.6224

Table III. Experimental Relative Peak Area and Molar Ratio for 2-Butanol

	First			Second			
M_{rel}	A_{hexane}	$A_{2\text{-butanol}}$	A_{rel}	A_{hexane}	$A_{2\text{-butanol}}$	A_{rel}	Mean A_{rel}
0.4954	1537432.49	390218.13	0.2538	475681.93	101729.91	0.2139	0.2339
0.8384	1865413.7	829305.52	0.4446	2763669.49	1268276.12	0.4589	0.4518
1.5535	3078503.99	2660761.54	0.8643	2547302.81	2055024.63	0.8067	0.8355
2.6974	1302119.45	1967207.17	1.5108	1304261.69	1918686.79	1.4711	1.4910
3.5375	1039490.8	2224033.77	2.1395	801088.09	1889223.29	2.3583	2.2489

Table IV. Experimental Relative Peak Area and Molar Ratio for 3-Methy-butanol

	First			Second			
M_{rel}	A_{hexane}	$A_{3\text{-methy-butanol}}$	A_{rel}	A_{hexane}	$A_{3\text{-methy-butanol}}$	A_{rel}	Mean A_{rel}
0.5367	1737904.1	633414.37	0.3645	1971003.44	700333.6	0.3553	0.3599
0.9998	2581765.0	1739902.94	0.6739	2629907.5	1911055.36	0.7267	0.7003
1.9773	2050853.07	2456675.1	1.1979	2163688.06	3624835.52	1.6753	1.4366
2.5332	1268339.04	2680937.12	2.1137	1726676.65	3276419.56	1.8975	2.0056
4.0833	1411451.81	4564050.66	3.2336	199500.02	609612.2	3.0557	3.1447

Table V. Experimental Relative Peak Area and Molar Ratio for 2-Methy-2-butanol

	First			Second			
M_{rel}	A_{hexane}	$A_{2\text{-methy-2-butanol}}$	A_{rel}	A_{hexane}	$A_{2\text{-methy-2-butanol}}$	A_{rel}	Mean A_{rel}
0.5297	2154371.23	857617.44	0.3981	2305010.85	968761.23	0.4203	0.4092
1.0571	1330024.26	1074317.18	0.8076	1128376.37	881757.37	0.7814	0.7945
1.9597	2649561.23	4259272.87	1.6075	2382968.86	3725547.83	1.5634	1.5855
2.8645	1842437.55	4611732.69	2.5031	1953379.28	4817941.89	2.4665	2.4848
3.9794	876742.45	2967699.82	3.3849	876630.32	3190496.05	3.6395	3.5122

Table VI. Experimental Relative Peak Area and Molar Ratio for 2-Pentanol

	First			Second			
M_{rel}	A_{hexane}	$A_{2\text{-pentanol}}$	A_{rel}	A_{hexane}	$A_{2\text{-pentanol}}$	A_{rel}	Mean A_{rel}
0.4162	2376277.78	496240.35	0.2088	2152932.16	465869.63	0.2164	0.2126
1.1489	2794123.78	1992047.15	0.7129	3092919.53	2271464.83	0.7344	0.7237
1.8212	1635327.36	2155700.47	1.3182	1815654.72	2429094.39	1.3379	1.3281
3.0255	1385690.06	3262292.87	2.3543	1151648.25	2779425.60	2.4134	2.3839
3.3856	1391280.30	3608329.91	2.5935	1432280.72	3712372.67	2.5919	2.5927

Table VII. Experimental Relative Peak Area and Molar Ratio for 3-Pentanol

	First			Second			
M_{rel}	A_{hexane}	$A_{3\text{-pentanol}}$	A_{rel}	A_{hexane}	$A_{3\text{-pentanol}}$	A_{rel}	Mean A_{rel}
0.4946	1892488.72	514553.40	0.2719	1779807.43	468379.31	0.2632	0.2676
0.9591	1385578.66	906096.91	0.6539	2226756.18	1379624.11	0.6196	0.6368
2.1642	1200002.73	2270461.29	1.8920	1202083.43	2128868.87	1.7710	1.8315
2.8309	1314012.35	2878286.93	2.1905	1468471.53	3300729.22	2.2477	2.2191
3.5095	1270826.08	3506776.18	2.7594	1251578.26	3491106.65	2.7894	2.7744

Table VIII. Experimental Relative Peak Area and Molar Ratio for Hexanol

	First			Second			
M_{rel}	A_{hexane}	$A_{hexanol}$	A_{rel}	A_{hexane}	$A_{hexanol}$	A_{rel}	Mean A_{rel}
0.5070	1711872.75	482396.20	0.2818	1784676.34	437903.61	0.2454	0.2636
0.9864	2006843.80	1365766.71	0.6806	2483018.22	1905906.13	0.7676	0.7241
1.9995	1498462.15	2826067.25	1.8860	1611802.85	2957080.36	1.8346	1.8603
3.0489	1128409.02	3123344.75	2.7679	1137761.58	3206651.24	2.8184	2.7932
3.6119	896070.91	3010989.28	3.3602	977287.86	3355375.69	3.4334	3.3968

Table IX. Experimental Relative Peak Area and Molar Ratio for Cyclohexanol

	First			Second			
M_{rel}	A_{hexane}	$A_{cyclohexanol}$	A_{rel}	A_{hexane}	$A_{cyclohexanol}$	A_{rel}	Mean A_{rel}
0.2499	4406547.53	590255.95	0.1339	3366009.83	503505.19	0.1496	0.1418
0.3176	3223880.89	580554.01	0.1801	3170242.87	553755.78	0.1747	0.1774
0.4891	4369176.88	1361773.27	0.3117	3894652.43	937807.03	0.2408	0.2762
1.1199	2645768.14	2635289.01	0.9960	1629723.04	1806210.36	1.1083	1.0522
2.0958	1691532.68	3441284.65	2.0344	1648716.33	3429485.92	2.0801	2.0573

Table X. Experimental Relative Peak Area and Molar Ratio for Heptanol

	First			Second			
M_{re}	A_{hexane}	$A_{heptanol}$	A_{rel}	A_{hexane}	$A_{heptanol}$	A_{rel}	Mean A_{rel}
0.5432	2234912.55	786559.68	0.3519	2222432.26	807394.50	0.3633	0.3576
0.9488	1657016.49	1298920.88	0.7839	1850195.59	1399052.04	0.7562	0.7701
1.9572	1743359.66	2911183.38	1.6699	1634089.90	2827889.00	1.7306	1.7003
2.8200	1135631.73	3091875.43	2.7226	1128422.19	3007666.59	2.6654	2.6940
3.4554	861973.34	3062078.73	3.5524	915948.84	3236711.80	3.5337	3.5431

Table XI. Experimental Relative Peak Area and Molar Ratio for Octanol

	First			Second			
M_{rel}	A_{hexane}	$A_{octanol}$	A_{rel}	A_{hexane}	$A_{octanol}$	A_{rel}	Mean A_{rel}
0.4734	1488929.28	371727.83	0.2497	1684869.48	474398.78	0.2816	0.2657
0.9852	1783039.56	1818359.21	1.0198	1867703.70	1889535.30	1.0117	1.0158
2.1391	1332189.67	3042956.43	2.2842	1260513.53	2866512.18	2.2741	2.2792
2.5742	1310625.49	3462324.83	2.6417	1020900.06	2804802.26	2.7474	2.6946
3.5073	949579.49	3489461.58	3.6747	1119126.87	4425367.65	3.9543	3.8145

Table XII. Experimental Relative Peak Area and Molar Ratio for Chlorobutane

	First			Second			
M_{rel}	A_{hexane}	$A_{chlorobutane}$	A_{rel}	A_{hexane}	$A_{chlorobutane}$	A_{rel}	Mean A_{rel}
0.2509	3899054.47	536789.69	0.1377	4981179.5	689272.4	0.1384	0.1380
0.3343	2535673.49	475452.57	0.1875	4212757.39	817424.1	0.1940	0.1908
0.4885	1729798.38	491508.71	0.2841	2732066.38	806242.62	0.2951	0.2896
0.9988	561617.05	339592.23	0.6047	71740.28	43298.54	0.6035	0.6041
2.0113	3569371.5	4163920.33	1.1666	2661022.63	3286226.28	1.2349	1.2008

Table XIII. Experimental Relative Peak Area and Molar Ratio for Chloropentane

	First			Second			
M_{rel}	A_{hexane}	$A_{chloropentane}$	A_{rel}	A_{hexane}	$A_{chloropentane}$	A_{rel}	Mean A_{rel}
0.2606	2912738.56	523238.61	0.1796	2594041.52	467700.12	0.1803	0.1800
0.4092	3496464.74	1049709.34	0.3002	2693067.56	769590.83	0.2858	0.2930
0.5134	3633849.49	1429014.12	0.3933	2981359.12	1159338.14	0.3889	0.3911
1.0401	1623193.83	1258135.03	0.7751	1758316.34	1393968.35	0.7928	0.7839
2.2788	1724495.63	2839810.53	1.6467	1792160.98	2911481.35	1.6246	1.6357

Table XIV. Experimental Relative Peak Area and Molar Ratio for 2-Chloropentane

	First			Second			
M_{rel}	A_{hexane}	$A_{2\text{-chloropentane}}$	A_{rel}	A_{hexane}	$A_{2\text{-chloropentane}}$	A_{rel}	Mean A_{rel}
0.1987	1029555.87	151685.61	0.1473	1061231.68	153833.63	0.1450	0.1461
0.2335	977379.21	167288.43	0.1712	878437.34	148257.16	0.1688	0.1700
0.3417	1003178.91	242639.26	0.2419	1432465.02	333049.05	0.2325	0.2372
0.7685	548991.91	313542.61	0.5711	843385.99	469470.82	0.5567	0.5639
1.4246	957881.65	1032816.23	1.0782	1091009.66	1165662.64	1.0684	1.0733

Table XV. Experimental Relative Peak Area and Molar Ratio for 3-Methy-chlorobutane

	First			Second			
M_{rel}	A_{hexane}	$A_{3\text{-methy-chlorobutane}}$	A_{rel}	A_{hexane}	$A_{3\text{-methy-chlorobutane}}$	A_{rel}	Mean A_{rel}
0.2883	2970875.69	622056.07	0.2094	3659518.71	788959.00	0.2156	0.2125
0.3225	2349886.84	541165.23	0.2303	4468671.83	1129992.02	0.2529	0.2416
0.4790	1512404.18	497391.85	0.3289	2813771.56	1000023.33	0.3554	0.3421
0.9801	1714016.85	1293366.79	0.7546	2115165.4	1592630.99	0.7530	0.7538
1.6707	1756931.8	2441593.05	1.3897	1887304.76	2665183.27	1.4122	1.4009

Table XVI. Experimental Relative Peak Area and Molar Ratio for Chlorohexane

	First			Second			
M_{rel}	A_{hexane}	$A_{chlorohexane}$	A_{rel}	A_{hexane}	$A_{chlorohexane}$	A_{rel}	Mean A_{rel}
0.2517	322997.54	53223.9	0.1648	103757.81	23865.27	0.2300	0.1974
0.3301	354271.46	84883.29	0.2396	1022228.13	307611.16	0.3009	0.2703
0.4978	115066.77	48530.98	0.4218	923336.42	364942.25	0.3952	0.4085
0.9723	717776.3	683649.73	0.9525	1758533.42	1609013.46	0.9150	0.9337
1.7030	708863.39	1157221.46	1.6325	159798.42	256467.02	1.6049	1.6187

Table XVII. Experimental Relative Peak Area and Molar Ratio for Cyclochlorohexane

	First			Second			
M_{rel}	A_{hexane}	$A_{cyclochlorohexane}$	A_{rel}	A_{hexane}	$A_{cyclochlorohexane}$	A_{rel}	Mean A_{rel}
0.4095	3721765.86	1169257.83	0.3142	3418826.89	1060616.25	0.3102	0.3122
0.9788	2702493.69	2361684.58	0.8739	2307795.13	2017704.72	0.8743	0.8741
2.0399	2050312.53	4107298.14	2.0033	2568038.75	5047961.54	1.9657	1.9845
2.8934	1977296.05	5493370.14	2.7782	1943058.27	5389143.74	2.7735	2.7759
4.0546	1493772.82	5784712.52	3.8726	1483481.05	5845384.03	3.9403	3.9065

Table XVIII. Experimental Relative Peak Area and Molar Ratio for Chlorooctane

	First			Second			
M_{rel}	A_{hexane}	$A_{chlorooctane}$	A_{rel}	A_{hexane}	$A_{chlorooctane}$	A_{rel}	Mean A_{rel}
0.2929	1847769.06	494099.35	0.2674	1979594.91	462860.5	0.2338	0.2506
0.3022	2875356.12	772330.98	0.2686	806348.79	197035.28	0.2444	0.2565
0.4205	1552794.86	687735.4	0.4429	1319691.04	396964.09	0.3008	0.3719
0.9789	726105.34	676946.86	0.9323	1002577.41	1057014.04	1.0543	0.9933
1.7126	1057563.93	1816930.54	1.7180	1910693.26	2963575	1.5510	1.6345

Table XIX. Experimental Relative Peak Area and Molar Ratio for Amylamine

	First			Second			
M_{rel}	A_{hexane}	$A_{amylamine}$	A_{rel}	A_{hexane}	$A_{amylamine}$	A_{rel}	Mean A_{re}
0.4501	2594265.39	295480.67	0.1139	3202684.98	350078.12	0.1093	0.1116
1.0495	3384810.42	2221946.37	0.6564	2958452.64	1780336.22	0.6018	0.6291
2.3688	1622640.74	2311846.37	1.4247	1440323.37	2094629.97	1.4543	1.4395
2.5924	1192316.64	1836070.58	1.5399	1485796.73	2389393.34	1.6081	1.5740

Table XX. Experimental Relative Peak Area and Molar Ratio for 3-Methylbutylamine

	First			Second			
M_{rel}	A_{hexane}	$A_{3\text{-methylbutylamine}}$	A_{rel}	A_{hexane}	$A_{3\text{-methylbutylamine}}$	A_{rel}	Mean A_{rel}
0.4414	2861636.53	446801.43	0.1561	3769270.53	599692.62	0.1591	0.1576
0.9627	3620657.73	2033336.24	0.5616	3787976.62	2082849.07	0.5499	0.5558
2.3169	2039992.73	2484606.08	1.2179	2214097.91	2834259.87	1.2801	1.2490
2.9505	1993051.86	3721404.54	1.8672	1942020.22	3688495.67	1.8993	1.8833
3.5237	1827983.36	4162502.82	2.2771	1897020.65	4422978.10	2.3315	2.3043

Table XXI. Experimental Relative Peak Area and Molar Ratio for Hexylamine

	First			Second			
M_{rel}	A_{hexane}	$A_{hexylamine}$	A_{rel}	A_{hexane}	$A_{hexylamine}$	A_{rel}	Mean A_{rel}
0.4650	3161697.97	467267.00	0.1478	2473563.25	312452.55	0.1263	0.1371
0.8850	1896177.24	667114.24	0.3518	2165608.42	911576.25	0.4209	0.3864
1.9465	1699367.48	1874344	1.1030	1114050.27	1223942.73	1.0986	1.1008
2.9784	1340128.90	2606770.21	1.9452	1258442.22	2509266.80	1.9939	1.9696
3.4338	1267930.34	3175567.05	2.5045	1035422.22	2728638.06	2.6353	2.5699

Table XXII. Experimental Relative Peak Area and Molar Ratio for Hexanethiol

	First			Second			
M_{rel}	A_{hexane}	$A_{hexanethiol}$	A_{rel}	A_{hexane}	$A_{hexanethiol}$	A_{rel}	Mean A_{rel}
0.5295	1839893.63	454861.29	0.2472	2052110.89	556683.79	0.2713	0.2593
0.9839	1592405.75	893193.92	0.5609	1390681.83	772723.86	0.5556	0.5583
2.0294	1244830.93	1460211.98	1.1730	1186379.42	1429241.36	1.2047	1.1889
3.0140	1250950.54	2266963.77	1.8122	1101031.51	2050183.32	1.8621	1.8372
3.7949	1080566.26	2660482.73	2.4621	1172835.73	3439367.74	2.9325	2.6973

Table XXIII. Experimental Relative Peak Area and Molar Ratio for 3-Methylbutanethiol

	First			Second			
M_{rel}	A_{hexane}	$A_{3\text{-methylbutanethiol}}$	A_{rel}	A_{hexane}	$A_{3\text{-methylbutanethiol}}$	A_{rel}	Mean A_{rel}
0.4883	2572550.12	548383.82	0.2132	2378282.30	524368.75	0.2205	0.2169
1.0081	662128.87	292325.12	0.4415	917254.22	455112.85	0.4962	0.4689
1.8489	1295736.80	1291361.46	0.9966	1146525.21	1226629.19	1.0699	1.0333
2.8396	1199043.51	2148750.71	1.7921	1245928.34	2363738.65	1.8972	1.8447
4.6463	902632.77	2670025.16	2.9580	848359.01	2581394.89	3.0428	3.0004