

The Determination of GC–MS Relative Molar Responses of Some *n*-Alkanes and their Halogenated Analogs

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The dependence of relative response factors on the carbon atom number related to naphthalene has been investigated in homologous series by using gas chromatography–mass spectrometry. Relative responses of some straight chain aliphatic *n*-alkanes and their halogenated derivatives (chlorine, bromine and iodine) were compared in the experiments. Linear correlations were found between the molecular structures; i.e., the carbon atom number and relative molar response in current homologous series. In conclusion, mass spectrometric detection combined with gas chromatography was less sensitive to *n*-alkanes than to their derivatives containing a chlorine, bromine or iodine atom. After *n*-alkanes, mass spectrometric responses increase in the order of 1-chloroalkanes, 1-bromoalkanes and 1-iodoalkanes. These results are in accordance with electron ionization cross section data for *n*-alkyl-derivatives. The relative molar responses of the individual CH₂ groups are between 0.171 and 0.178 in the homologous series. The increments of chlorine, bromine and iodine atoms to the relative molar responses are 0.081, 0.141 and 0.492, respectively.

Based on these results, the additivity rule is valid for both halogen atoms and CH₂ groups in the case of mono-substituted *n*-haloalkanes. The results of this study show a significant departure from the additivity rule in the case of polyhalogenated alkanes and alkenes. However, the relative molar response can be calculated by means of simultaneously measuring other compounds. Further study is needed about how to influence the relative molar responses as a function of various experimental parameters.

Introduction

The application of mass spectrometric (MS) detection combined with gas chromatography (GC) and high-performance liquid chromatography (HPLC) separations is very popular and indispensable in daily analytical practice. This combination can provide required and sufficient analytical information, even about complicated samples. Qualitative information can be obtained by interpretation of mass spectra. The quantitative results can be originated from the measurement of the area under the gas chromatographic peak of the respective compound in the total ion current chromatogram (TIC). However, in both cases, particularly in quantitation, the use of suitable standard substances is important. Most are commercially available, but in many cases there are no standard materials of suitable quality in the market because they are difficult or impossible to synthesize. These are components of organic synthetic materials that are only present in the products of some technologies in one area percent quantity or fewer, but they

have to be taken into consideration in the mapping of the contamination profile during product qualification. In this case, the question is how an MS response factor can be calculated based on chemical structure without an available standard when a quantitative estimation is required.

In flame ionization detection (FID), the effective carbon number (ECN) has a direct correlation between response and molecular structure of the compounds, which makes quantitation estimates of structural homologous possible (1, 2, 3). The practical success of FID response estimation raises the need to investigate the functional connection between the molecular structure and the signal response for mass spectrometric detection. This is the focus of the current study.

Electron impact ionization (EI) ion source is typically used in GC–MS. For this technique, the component producing the ionic products is introduced into an energetic beam of electrons. The bigger ionization cross sections of the respective molecules, the higher probability that a sufficient impact of molecules and ion beam will be obtained. The cross section for the ionization of molecules or atoms can either be measured (4) or calculated. Concepts of the Deutsch-Mark formalism (5, 6, 7) have provided an efficient means for the determination of ionization cross sections. In addition to this semi-empirical model, there have been many attempts to model EI efficiency curves (the dependence of ionization cross section on electron energy) and theories for EI cross sections for atoms (4, 8), neutral molecules (9) and molecular ions (10, 11, 12). The Binary-Encounter-Bethe (BEB) model (10, 11) has successfully generated reliable total ionization cross sections of small and large molecules. However, the BEB model will require further refinements to expand its application to a wider class of molecules. Without experimental confirmation, these results can only be considered estimations. In the current study, model approaches were not utilized. The goal of our experiment was the determination of relative molar responses based solely on experimental data, according to analytical expectations.

The ionization cross sections of Alberti *et al.* (13) for *n*-alkanes and their derivatives were obtained by using the absolute value of the ionization cross section for argon from another experiment. Data can be found in literature for some hydrocarbons up to carbon atom number 6 (11, 14, 15), fragments of DNA (16), freons (17) and a few oxygenates (18). Data obtained in this manner are not suitable for the determination of relative response factors in daily routine analysis.

Quantitative analyses for GC–MS require up-to-date information about the working of the system to calculate exact

calibration curves for all compounds. There is an unbridgeable gap between the theories established for the determination of total ionization cross sections and the practice using the combined techniques. On one hand, the daily analytical results arise in part from measuring samples introduced directly into the mass spectrometer. On the other hand, the errors of GC-MS measurement can increase. To sum up, the use of ionization cross section data is more difficult than the relative molar responses obtained during daily routine analysis. Busch summarized the methods of quantitation in MS and directed our attention to some essential assumptions (19, 20, 21, 22, 23). According to this article series, quantitative determination requires the targeted compounds to be available as pure certified reference standards.

To solve the problem of accurate quantitative analysis, the primary question to be answered is how the sensitivity and relative sensitivity (relative molar response as related to naphthalene) depends upon the carbon atom number for each carbon in the skeleton, and the number and the quantity of function groups to produce the TIC chromatogram. The addition of a CH₂ group causes the same increment for the cross sections in a series of the investigated compounds (13). According to expectations, the relative molar responses change in the same way; thus, each compound in a homologous series can be determined by the known response of its other members. Based on this response principle of a homologous series, the response of the members of another series can be estimated when the correlation is known between the two groups. Many compounds do not have a homologous series response data available; however, correlations do exist and relative molar responses can be determined.

In this article, straight chain aliphatic alkanes and their halogenated (Cl, Br, I) derivatives have been investigated and compared with *n*-alkanes. The lists of compounds are shown in Table I.

Experimental

The concentrations of individual test compounds (straight chain aliphatic *n*-alkanes and their halogenated Cl, Br, I derivatives) were less than 10 mmol/mL in *n*-hexane solution. The concentrations were in linear range of the mass spectrometer. Mass measurements were conducted on a Shimadzu Libror AEL-40SM electronic analytical balance, and the mixed test solutions were investigated. In every case, naphthalene (Fluka,

≥ 99.7%) was used as an internal standard. Chemicals were analytical standards for GC from Fluka and Sigma-Aldrich. Each point of the results is the average of five consecutive measurements.

A Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer connection with a Shimadzu AOC 5000 auto injector was used. Compounds were separated on a 30 m × 0.25 mm i.d. × 0.25 μm Zebtron ZB-5 fused silica capillary column. Every measurement was performed under programmed temperature conditions: at 40°C for 3 min, temperature rate was 10°C/min up to 280°C, followed by a 9 min isothermal temperature part. The injector worked in split mode (split ratio 1:100) and its temperature was 360°C. The carrier gas was helium with a total flow of 163.0 mL/min, the flow rate on the column was 1.58 mL/min (linear velocity 45.4 cm/s) and the purge flow was 3.0 mL/min. The ion source temperature of the quadrupole mass spectrometer and the interface temperature was 200°C. Detector voltage was 1 kV and the electron energy applied to the system was 70 eV. The event scan time was 0.3 s. Taking the molecular weights of the investigated molecules into consideration, the mass scale was adjusted between mass to charge ratio (*m/z*) of 25–360.

Results and Discussion

As in previous studies (18, 24, 25, 26), at low pressures of EI experiments, the TIC is directly related to the ionization cross section, by the following equation:

$$\sum I_i^+ = Q_i I_e [n_i] d \quad (1)$$

where $\sum I_i^+$ is the total positive ion current, Q_i is the ionization cross section, $[n_i]$ is the concentration of sample molecules of species *i*, I_e is the electron current and *d* is the ionization path length.

For the calculation of relative molar response (RMR, relative sensitivity) in the present experiments, the following formula was used (27):

$$RMR_i = \frac{A_i n_j}{A_j n_i} \quad (2)$$

where RMR_i is the relative molar response of the investigated compound (*i*) related to the naphthalene (*j*), A_i is the area

Table I
Lists of Investigated Compounds

<i>n</i> -Alkanes	1-Bromoalkanes	1-Iodoalkanes	1-Chloroalkanes	Polyhalogenated compounds
<i>n</i> -Octane	1-Bromobutane	1-Iodopropane	1-Chloropentane	Dibromochloromethane
<i>n</i> -Nonane	1-Bromohexane	1-Iodobutane	1-Chlorohexane	Tetrachloroethylene
<i>n</i> -Decane	1-Bromoheptane	1-Iodopentane	1-Chloroheptane	Trichlorofluoromethane
<i>n</i> -Undecane	1-Bromooctane	1-Iodohexane	1-Chlorooctane	Perchloro-1,3-butadiene
<i>n</i> -Dodecane	1-Bromononane	1-Iodoheptane	1-Chlorononane	1,1,1,2-Tetrachloroethane
<i>n</i> -Tridecane	1-Bromodecane	1-Iodooctane	1-Chlorodecane	<i>cis</i> -1,3-Dichloropropene
<i>n</i> -Tetradecane	1-Bromoundecane	1-Iododecane	1-Chlorododecane	1,2-Dibromomethane
<i>n</i> -Hexadecane	1-Bromododecane	1-Iodododecane	1-Chlorooctadecane	1-Bromo-3-chloropropane
<i>n</i> -Heptadecane	1-Bromohexadecane	1-Iodoheptadecane		2,3-Dichloropropene
	1-Bromononadecane			1,1,2,2-Tetrachloroethane
				1,2-Dichloropropane

under the peak of the compound in TIC chromatogram (mVs), A_j is the area of naphthalene peak in TIC chromatogram (mVs), n_i and n_j are the concentrations (in mmol/mL or mmol) of the compound and naphthalene (in mmol/mL or mmol), respectively. Fundamental equations of quantitative analysis are: $A_i = S_i n_i$ and $A_j = S_j n_j$, where S_i and S_j are the individual sensitivities of the sample molecules and naphthalene. Mass spectra display the peaks for the molecules according to the mass range adjusted. The instrument scans the mass range per 0.3 s during the data acquisition. Every point in the chromatogram consists of the sum of all absolute intensities for m/z . The as-prepared chromatogram reconstructed by the computer is the TIC chromatogram. The connection between the relative molar response and the ionization cross sections is as follows:

$$RMR_i = \frac{A_i n_j}{A_j n_i} = \frac{S_i}{S_j} = \frac{Q_i}{Q_j} \quad (3)$$

As indicated previously, the cross sections were measured relative to different rare gases. In the present experiments, the reference material is unvaried, which provided an opportunity for uniform relative response factors. The internal standard method is used to compensate for the loss of analyte during the sample inlet and to eliminate random differences influencing the efficiency of ionization. Naphthalene has a very stable molecular ion with a mass of m/z 128. Other fragments of naphthalene have a small influence on mass spectral reactions; in practice, their molecular ion abundance provides the TIC chromatogram. Thus, naphthalene is used as a stable reference material.

Investigation of halogenated homologous series

The mass spectra of saturated straight-chain n -alkanes are very similar. Unfortunately, it is very difficult to find out which compound is actually visible in a given spectrum. In most cases, only the chromatographic retention order provides differentiation. The stabilization processes after the ionization of the molecule leads to a series of small masses, and even to electron numbers containing fragment ions with the general formulas of $C_n H_{2n-1}$ and $C_n H_{2n+1}$ (28). The mass spectrum of n -nonane describing the fragmentation behaviour is shown in Figure 1.

The correlation between the relative molar responses of respective compounds and the carbon atom number (n) is linear, as shown in Table II and Supplementary Figure 1. According to the fragmentations, the molecular ion plays only a minor part in the differences of relative molar response.

Alberti *et al.* (13) reported the ionization cross sections by electron impact for n -alkanes and their halogenated homologous series. A combined way to determine cross sections was chosen. First, the relative cross sections related to Ar were determined; then the absolute value was calculated, using the absolute cross section of Ar (this value was taken from the literature). The combination of the measured relative data and the actual non-measured cross section for Ar gives a systematic error. The present data were generated only from direct measurements. The individual relative intensities related to naphthalene were measured during the same experiment and the absolute cross section for naphthalene was not used. The relative molar response results determined in a different manner are in agreement with the tendency of values reported by Alberti *et al.* in Table III and Supplementary Figure 2. The highest values are given by 1-iodoalkanes, followed by 1-bromoalkanes, 1-chloroalkanes and n -alkanes in decreasing order according to the cross sections of halogen atoms substituted by hydrogen atoms. Table IV contains five consecutive measurements of 1-iodoalkanes, their means and their relative standard deviations (RSD). Other homologous series were calculated in the same way.

Alberti *et al.* (13) did not apply naphthalene as a reference material, so a direct comparison of slope data was not possible. However, some compounds were examined in common with his study and the current study. To compare cross section and RMRs with the current study's results, n -decane and its halogenated derivatives were chosen as temporary internal standards. By these means, the calculated data show slopes of lower value (0.082–0.092) than those values determined by the current study (0.099–0.128). These results are displayed in Table V. Despite the different bases from the two study measurements, the results were comparable. The current results display a higher relative sensitivity than those calculated by Alberti *et al.* (13). The ion source was the same in both studies, but a quadrupole analyzer was used instead of the double-focusing mass spectrometer used by Alberti *et al.* (13). Generally, quadrupole mass spectrometers provide lower resolution than double focusing instruments, but they tend to be more sensitive owing to the shorter ion pathway in the mass analyzer (higher ion transmission efficiency). These differences focus attention on the importance of experimental parameters. The use of cross sections or RMRs obtained from literature values will always need some correction due to different experimental conditions and instrumentation. The type of analyzer is only one parameter; ion source temperature, event scan time mass range and gas chromatographic setting may affect the values.

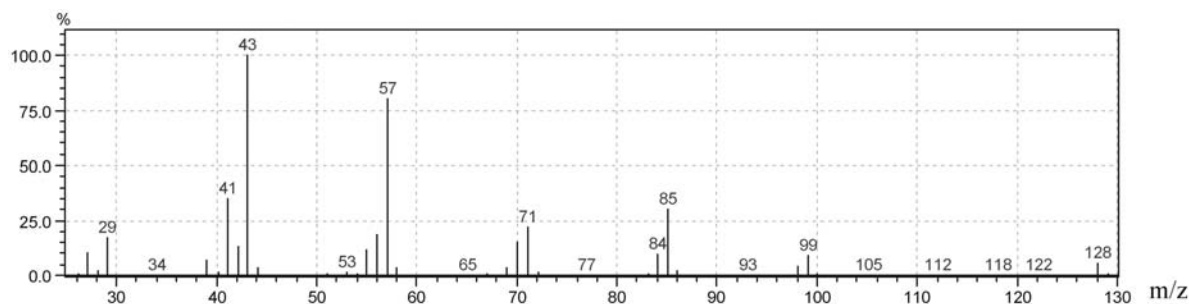


Figure 1. Mass spectrum of n -nonane.

Only the horizontal rows of Table V are comparable. The internal standard was varied along the vertical columns in this study; thus, any comparison will be in error. Differences between the slopes of homologous series from Alberti *et al.* (13) and these results were 0.033 (1-chloroalkanes), 0.036 (*n*-alkanes), 0.016 (1-bromoalkanes) and 0.017 (1-iodoalkanes). According to these differences, the relative molar responses of the CH₂ unit of *n*-alkanes and 1-chloroalkanes were approximately twice as high as 1-bromoalkanes and 1-iodoalkanes.

Table II

Correlation between Carbon Atom Number (*n*), RMRs and Increment of Halogens*

Name of group	Equation of curve	Regression coefficient	Increment of halogen atom to RMR
1-Iodoalkanes	$RMR = 0.178n + 0.087$	0.9897	0.492
1-Bromoalkanes	$RMR = 0.171n - 0.264$	0.9947	0.141
1-Chloroalkanes	$RMR = 0.171n - 0.324$	0.9991	0.081
<i>n</i> -Alkanes	$RMR = 0.171n - 0.405$	0.9920	—

*Note: The equations of 1-iodoalkanes, 1-bromoalkanes, 1-chloroalkanes and *n*-alkanes contain 9, 10, 8 and 9 points, respectively. One point consists of 5 consecutive measurements.

Table III

Correlation between *n* and EI cross sections (*Q*) (13)*

Name of group	Equation of curve	Regression coefficient
1-Iodoalkanes	$Q = 2.470n + 5.487$	0.9996
1-Bromoalkanes	$Q = 2.445n + 4.747$	0.9999
1-Chloroalkanes	$Q = 2.441n + 3.547$	0.9993
<i>n</i> -Alkanes	$Q = 2.440n + 2.031$	0.9999

*Note: The equations of 1-iodoalkanes, 1-bromoalkanes, 1-chloroalkanes and *n*-alkanes contain 10, 14, 10 and 13 measured points, respectively.

The RMR of the individual CH₂ group related to naphthalene has very similar values in the investigated homologous series. The slopes of the lines are between 0.171 and 0.178 in Table II. This means that the different halogen substitutions are indicated in differences between the intercepts of the lines. These differences are the increments of halogen atoms to the RMR of halogen-substituted *n*-alkanes. The value of this increment is as follows: chlorine is $-0.324 - (-0.405) = 0.081$, bromine is $-0.264 - (-0.405) = 0.141$ and iodine is $0.087 - (-0.405) = 0.492$ (Table II). Based on these results, the additivity rule is valid for both halogen atoms and CH₂ groups in the cases of mono-substituted *n*-haloalkanes.

The investigated compounds in Figures 2–4 show that the fragmentation patterns of halogenated compounds are very similar to the *n*-alkanes. This is why the RMRs taken as a function of the carbon atom number of *n*-alkanes and 1-iodoalkanes increase in the same way. The stream of vaporized sample molecules entering the ion source interacts with the beam of electrons to form a variety of products; first, the molecular ion, which is unstable in the cases of *n*-alkanes and alkyl halides. Thus, these ions do not take a prominent part in the mass spectra and the signal formations. The molecular ion of 1-iodoalkanes loses neutral and radical iodine in a quick step and the positive charged residue fragments as *n*-alkanes. The primary fragments and their ratios providing the gas chromatographic peak are the same in the related mass spectra (Figure 2).

Bromine has higher electronegativity than iodine, which is why it prefers forming the bromide ion as the hydrogen bromide molecule to cleaving as a neutral radical. The residue after the cleavage of hydrogen bromide shows a fragmentation pathway similar to that of *n*-alkanes. However, another

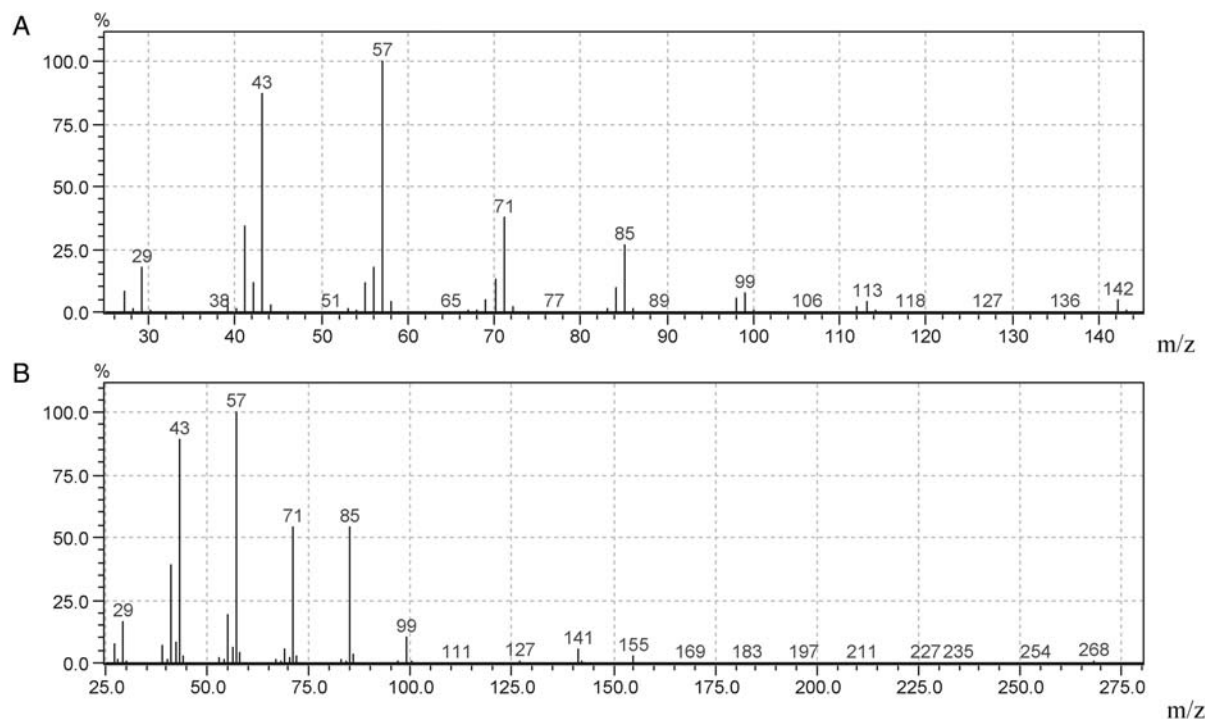


Figure 2. Mass spectra of *n*-decane (A) and 1-iododecane (B).

molecular ion stabilization process appears in parallel with the elimination reaction, which is the formation of $C_4H_8Br^+$ with enhanced stability. The primary difference, shown in Figure 3,

Table IV

Relative Response Factors of 1-Iodoalkanes*

Compound name	RMR ₁	RMR ₂	RMR ₃	RMR ₄	RMR ₅	Mean of RMR	RSD%	ΔRMR
1-Iodopropane	0.578	0.573	0.578	0.573	0.562	0.573	1.13	0.191
1-Iodobutane	0.719	0.722	0.724	0.726	0.720	0.722	0.40	0.181
1-Iodopentane	0.932	0.941	0.934	0.932	0.925	0.933	0.62	0.187
1-Iodohexane	1.175	1.175	1.170	1.169	1.167	1.171	0.28	0.195
Naphtalene	1.000	1.000	1.000	1.000	1.000	1.000	0.00	
1-Iodoheptane	1.503	1.462	1.493	1.459	1.459	1.475	1.44	0.211
1-Iodooctane	1.508	1.520	1.523	1.525	1.511	1.517	0.48	0.190
1-Iododecane	1.899	1.931	1.911	1.977	1.963	1.936	1.71	0.194
1-Iodododecane	2.184	2.240	2.193	2.313	2.337	2.253	3.08	0.188
1-Iodohexadecane	2.742	2.850	2.770	2.920	2.913	2.839	2.86	0.177

*Note: The table contains five consecutive measurements, their means and their RSDs. The deviation in relative molar responses from respective *n*-alkanes is shown in the ΔRMR column.

Table V

Correlation between *n* and RMR

Name of group*	Equation of curve [†]	Equation of curve [‡]	Difference of slopes
<i>n</i> -Alkanes	$RMR = 0.092n + 0.077$	$RMR = 0.128n - 0.303$	0.036
1-Iodoalkanes	$RMR = 0.082n + 0.181$	$RMR = 0.099n + 0.003$	0.017
1-Bromoalkanes	$RMR = 0.084n + 0.163$	$RMR = 0.100n - 0.033$	0.016
1-Chloroalkanes	$RMR = 0.087n + 0.127$	$RMR = 0.120n - 0.227$	0.033

*Internal standards are *n*-decane, 1-iododecane, 1-bromodecane and 1-chlorodecane, respectively, for *n*-alkanes, 1-iodoalkanes, 1-bromoalkanes and 1-chloroalkanes.

[†]Data from Alberti *et al.* (13).

[‡]Present results.

is the presence of m/z 135 (and m/z 137, according to the abundance of bromine isotopes). The other major parts of 1-bromoalkanes of the mass spectrum seem to follow the fragmentation patterns of *n*-alkanes. Due to the enhanced stability of m/z 135, the 1-bromoalkanes show higher relative response factors than the *n*-alkanes.

The mass spectra of 1-chloroalkanes show significant differences compared to *n*-alkanes. In addition to the characteristic fragments of *n*-alkanes, a specific mass forms in the ion source. Similar to 1-bromoalkanes, the molecules decompose in part by the loss of $C_4H_8Cl^+$ of m/z 91. Due to the stability of m/z 91, the relative response factors are higher than those of *n*-alkanes, as in the case of former 1-bromoalkanes.

Regarding the 1-bromoalkanes, the sum of the absolute intensities of ions of only one mass spectrum without $C_4H_8Br^+$ intensity, related to the total absolute intensity, is between 0.85–0.87. However, the situation is the same in the case of 1-chloroalkanes, but the values are slightly smaller, between 0.74–0.76, without $C_4H_8Cl^+$.

The results of the additivity of RMR in homologous series lead to the expectation of future investigation and study of other families of compounds of more practical analytical importance to determine their RMR.

Investigation of polyhalogenated *n*-alkanes and *n*-alkenes

In connection with the investigation of homologous series, some polyhalogenated *n*-alkanes and *n*-alkenes were analyzed. In a previous study (26), EI cross sections were measured for 62 hydrocarbons, fluorocarbons and halogen-substituted hydrocarbons. The ionization cross sections for these molecules

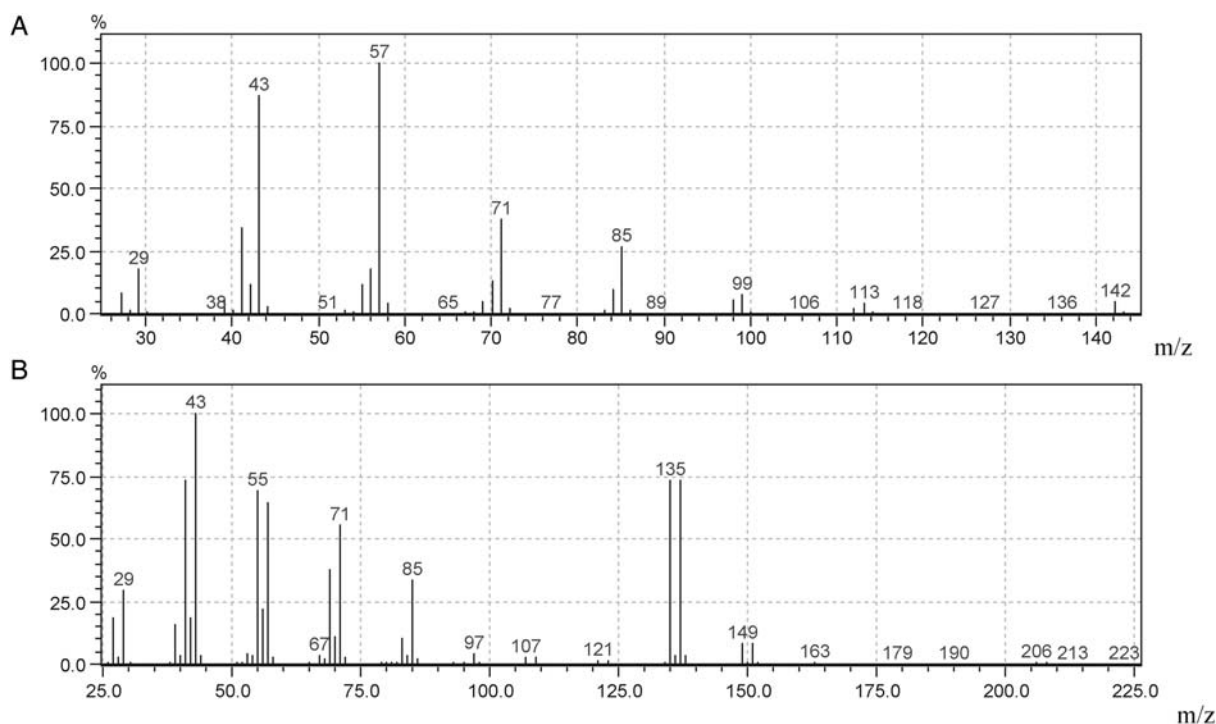


Figure 3. Mass spectra of *n*-decane (A) and 1-bromodecane (B).

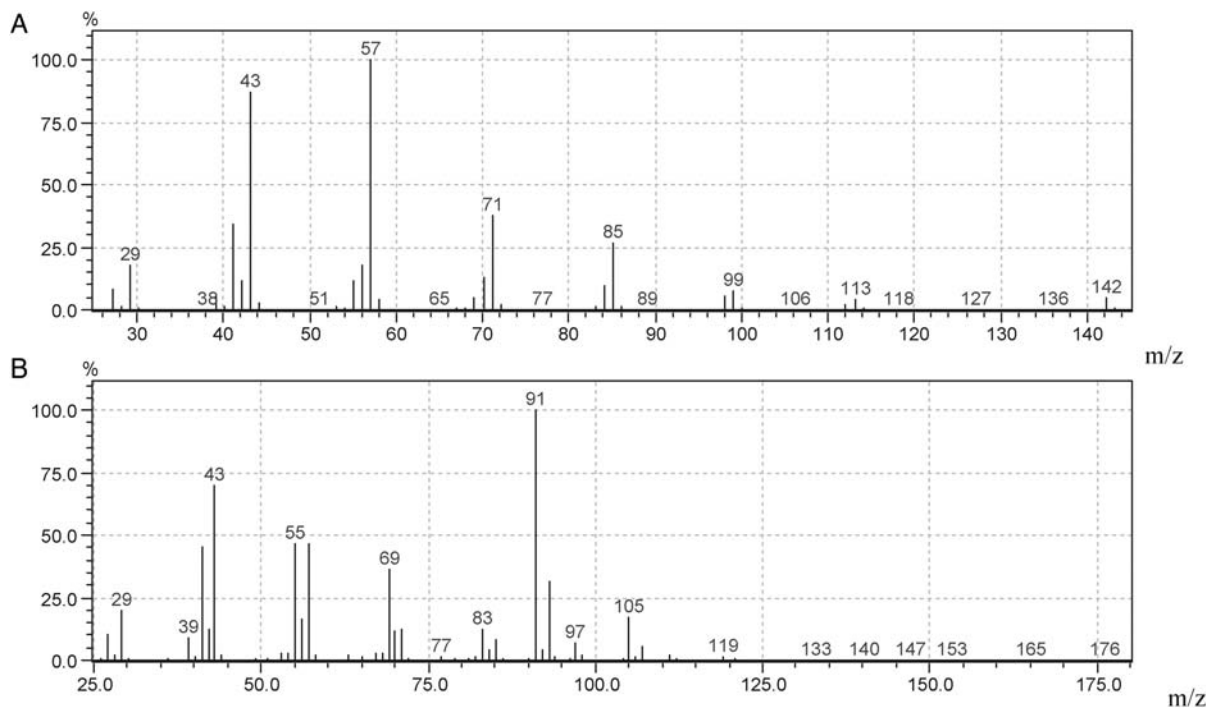


Figure 4. Mass spectra of *n*-decane (A) and 1-chlorodecane (B).

indicate diversity and no correlation can be obtained either in the function of carbon atom number or the halogen atom number, which is because they belong to different homologous series. The interesting question is whether a correlation exists between other molecules. These compounds are summarized in Table VI in the increasing order of RMRs. The isomer compounds consist of the same atoms in the same number. The RMRs of 1,2-dichloropropane (RMR = 1.058) and 1,3-dichloropropane (RMR = 0.848) should be identical based on the principle of the ionization cross section, but they do not fit a simple additivity postulate. Their fragmentation patterns are not similar (Figure 5) because the different fragments and abundances indicate different RMRs. 2,3-Dichloropropene (RMR = 0.781) and *cis*-1,3-dichloropropene (RMR = 0.689) also show differences. The MS detector gives a higher ionization cross section for the *n*-alkanes than the *n*-alkenes (26). 1,1,1,2-Tetrachloroethane (RMR = 0.638), 1,1,2,2-tetrachloroethane (RMR = 0.947) and tetrachloroethylene (RMR = 0.528) are in accordance with these results. 1,2-Dichloropropane (RMR = 1.058), 1,3-dichloropropane (RMR = 0.848) and *cis*-1,3-dichloropropene (RMR = 0.689) also keep this rule; however, 2,3-dichloropropene (RMR = 0.781) does not follow the *n*-alkanes and *n*-alkenes.

It is an important observation that an additivity rule cannot easily be established. Due to the isomers, the addition of more than one chlorine, bromine or iodine atom does not mean permanent differences. Otvos and Stevenson set up the additivity rule for the determination of the molecular electron ionization cross section based on the cross sections of building atoms (18). However, this rule contains numerous corrections considering the molecular bonds. Furthermore, the sum of the EI cross sections of atoms does not easily

Table VI

Relative Response Factor Values for Polyhalogenated *n*-Alkanes and *n*-Alkenes

Compound name	RMR	Number of halogens	<i>n</i>
Dibromochloromethane	0.416	3	1
Tetrachloroethylene	0.528	4	2
Trichlorofluoromethane	0.578	4	1
Perchloro-1,3-butadiene	0.617	6	4
1,1,1,2-Tetrachloroethane	0.638	4	2
<i>cis</i> -1,3-Dichloropropene	0.689	2	3
1,2-Dibromomethane	0.751	2	2
1-Bromo-3-chloropropane	0.775	2	3
2,3-Dichloropropene	0.781	2	3
1,3-Dichloropropane	0.848	2	3
1,1,2,2-Tetrachloroethane	0.947	4	2
1,2-Dichloropropane	1.058	2	3

provide the molecular value. Similar to this problem, the MS responses of investigated molecules are not provided in a simple way.

According to the measurements of this study (and other not yet published results by this laboratory) and published literature data, the relative molar response and cross sections were not accurately predicted for polyhalogenated compounds. However, the relative molar response can be estimated with the assistance of other simultaneously measured compounds. In this way, the measurement conditions can be eliminated and the difference between the two RMRs would be constant. The measurement conditions remain an important consideration. The effect of experimental conditions upon RMRs is the topic of further study.

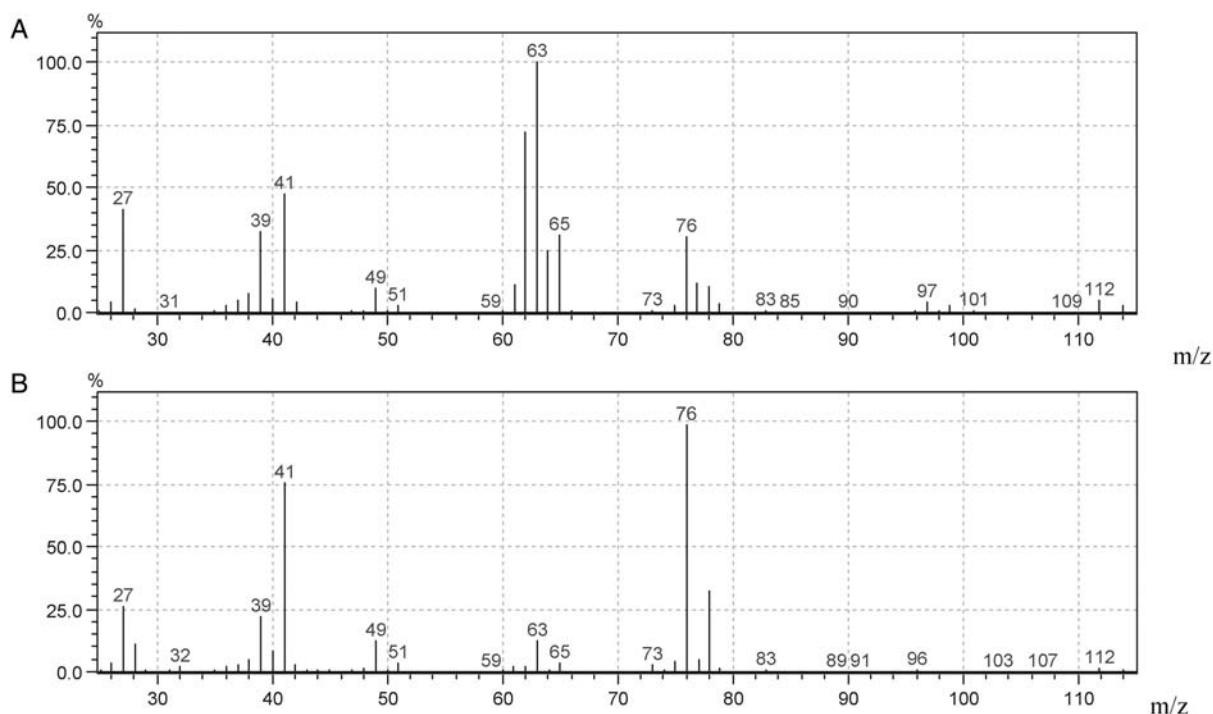


Figure 5. Mass spectra of 1,2-dichloropropane (A) and 1,3-dichloropropane (B).

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Supplementary data

Supplementary data is available at *Journal of Chromatographic Science* online.

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