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## Molecular mass and location of the most abundant peak of the molecular ion isotopomeric cluster

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**Abstract** The location of the most abundant peak of the molecular-ion pattern often differs from the molecular mass published in scientific databases. The location is also distinct from the value expected from average atomic masses. The cause of this phenomenon is a large number of atoms of carbon, sulfur, chlorine, bromine, silicon and boron. This due to the natural isotope abundances of some elements forming organic compounds. A parameter called location of the most abundant peak of an isotopometric cluster (LAPIC) denotes the location of the most abundant (the main) peak of an isotopomeric cluster, which is determined, e.g., by mass spectrometry and can be important for medium- and high-molecular mass compounds. The equations for LAPIC calculation are presented for elements usually observed in organic compounds. The LAPIC with elemental formula helps effectively, e.g., in mass spectra interpretation since the prediction of LAPIC allows the correct connection of the main peak of the investigated ion with the expected ion formula and the mass of the ion considered. This solution can be a substitute for the much more complex method of isotopometric analysis applied in mass spectra interpretation.

**Keywords** Molecular ion · Molecular mass · Isotopomeric cluster · Cluster modeling · Mass spectrometry

### Introduction

The formula of a compound and its molecular mass are significant features for investigations of recently isolated natural substances as well as newly synthesized ones.

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These parameters can be determined precisely by mass spectral investigations. The intensities and locations of peaks belonging to a molecular cluster<sup>1</sup> allow the determination of the molecular mass and formula of a compound. The relations between the intensities of the molecular peak  $M^+$  and isotopomeric peaks  $(M + 1)^+$  and  $(M + 2)^+$  are a starting point for molecular formula investigations of organic compounds containing C, H, N, O, F, I and P [1–4]. The elements commonly occurring in organic compounds usually have one single isotope or one isotope is dominant [5, 6]. The determination of molecular formulae is more difficult for organic compounds with B, Cl, Br, S and Si. The theoretical calculation of molecular bands presented by Beynon [2, 7] solved this problem for compounds containing up to ten atoms of B, S and Si and up to eight atoms of Br and Cl, alone or in combination. For this reason, the molecular formulae of such compounds can be determined easily from isotopomeric peak intensities. Attempts to understand the molecules containing such heteroatoms face difficulties due to the complexity of the isotopomeric composition of the molecule considered.

On the other hand, the relative peak intensities of peaks forming the cluster may be predicted from the molecular formula and the isotopic abundance ratios of the constituent elements [8–10]. The natural isotopic abundance of each element is represented by a polynomial expression [11–13]. Calculations entail a successive expansion of polynomials in which each polynomial represents one element of the molecular formula. The exponent value of each polynomial is equal to the number of atoms of that element in the formula. Molecular patterns of organic compounds are characterized by a small isotopomeric width—width of isotopomeric cluster (WIC) [14]. Simple organic compounds show a few isotopomeric peaks only, and their molecular ion pattern usually contains three peaks or fewer [4].

<sup>1</sup>Clusters, patterns or bands—well separated (valley = 0%) parts of mass spectra containing several peaks, usually distanced by 1 unit of  $m/z$ .

The determination of the molecular formula is the principal point of interpretation of the molecular pattern. Usually the location of the main peak of the band investigated is the base for the hypothesis of summary formula of the ion. Low abundance isotopes, which do not play a significant role in low-mass compounds, can make significant contributions to the mass spectral pattern related to medium or high mass compounds.

For example,  $^{13}\text{C}$  contributes only 1.1% relative to  $^{12}\text{C}$  in nature. In the styrene molecular ion  $\text{C}_8\text{H}_8^+$ , the most abundant isotopomeric peak is at  $m/z$  104 and the ion contains only  $^{12}\text{C}$  atoms. The abundance of the  $(M + 1)^+$  ion containing one  $^{13}\text{C}$  atom is 8.8% of the most abundant isotopic peak. However, for polystyrene with a degree of polymerization of 100 ( $\text{C}_{804}\text{H}_{810}$ ), the isotopomeric peak containing one  $^{13}\text{C}$  atom is about nine times more abundant than the isotopomeric peak containing only  $^{12}\text{C}$  atoms. The main peak of the molecular cluster of this polymer is located at  $m/z = 10467$ , and suggests the formula  $\text{C}_{804}\text{H}_{819}$ . The number of hydrogen atoms in such a compound is false, as the most abundant ionic species in the molecular cluster has a formula  $^{12}\text{C}_{795}^{13}\text{C}_9\text{H}_{810}$  [15, 16]. As seen, neglecting the natural isotopic abundance can result in a false number of hydrogen atoms in a molecule and in real problems with structure elucidation. The isotopomeric pattern predicted from the parameters of the natural isotopes abundance recommended officially by IUPAC [6] is the same as the experimental one.

Parameters such as nominal mass<sup>2</sup> and mono-isotopic mass<sup>3</sup> used by Yergey [17] are not applicable for medium- and high-mass compounds, which usually produce wide isotopometric patterns [18]. Other parameters such as the most abundant mass<sup>4</sup> and average mass<sup>5</sup> better characterize the location of the “centroid” cluster,<sup>6</sup> but they result from complex coincidences of isotopic components. The “centroid” [17] denotes the form of a wide isotopic cluster observed for organometallic and coordination compounds as well as for medium- and high-mass organic compounds.

The element formula of each compound or ion can be regarded as the sum of elemental aggregates of mono-isotopic elements, such as hydrogen, iodine, fluorine, phosphorus and the isotopic elements,<sup>7</sup> such as carbon, sulfur, bromine, chlorine, silicon and so on, e.g., the

formula of organic compound such as the methyl ester of etamycine acid is an adduct of four agglomerates:<sup>8</sup>

$$\text{C}_{45}\text{H}_{66}\text{N}_8\text{O}_{12} = (\text{C})_{45} + (\text{H})_{66} + (\text{N})_8 + (\text{O})_{12} \quad (1)$$

Elements of the first group (H, I, F and P) are isotopically neutral and the location of the most abundant molecular peak (the main one of molecular cluster) corresponds to the  $m/z$  value expected from the nominal atomic masses. The occurrence of the second group elements (B, Br, C, Cl, S and Si) results in a complex form of the ion cluster. The isotopic element aggregates significantly influence two classes of the isotopic pattern parameters, as follows:

- location: locations ( $m/z$ ) of the cluster, the most abundant peak and other peaks of the pattern; and
- form: width of isotopomeric cluster [14], number of peaks forming the cluster and their intensities (e.g., RI in %) of the individual peaks.

Such parameters can provide valuable information for experienced scientists, but their determination requires the application of multi-isotopomeric analysis.

The current work presents a new application of isotopomeric analysis for the determination of contents and form of the cluster. This paper describes the locations of the main peak of isotopomeric clusters as a function of the number of atoms contained in the element aggregates for the elements usually forming organic compounds. All calculations used by the multisotopomeric modeling of ion pattern (MMIP) method [11–13], which is based on natural isotopes abundances, recommended by IUPAC [6]. This method should be an efficient aid for interpretation of MS spectra.

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### The most abundant peak of the isotopomeric cluster

The form of the isotopomeric cluster may be used for ion formula determination, but this approach is really difficult [3, 4]. Beynon's calculations show the unexpectedly serious difficulties occurring in halogen derivatives [7] (Cl and/or Br). The increased number of isotopic element atoms in medium- or high-molecular compounds leads to complex molecular patterns. The isotopic species of the single atoms and isotopomeric profiles of element aggregates are compared in Fig. 1.

The upper graphic row contains pictures of single atom clusters  $(\text{Elem})_1$  for boron, bromine, carbon, chlorine, sulfur and silicon. Usually, one of the isotope forms is dominant (except Br, for which the contributions of both natural isotopes are approximately equal). The lower pictorial row presents a view of centroidal patterns of  $(\text{Elem})_n$  aggregates. The locations of the most abundant peak of the corresponding clusters are summarized in numeric rows containing main peak locations in  $m_i/z$  with intensities  $P_i$ . The numbers of

<sup>2</sup>Nominal mass, calculated for molecular ion by using the most abundant isotope of each element, without regard for the mass defect.

<sup>3</sup>Mono-isotopic mass, which refers to the molecular ion peak composed from the most abundant isotopes of the elements, but includes the mass defect

<sup>4</sup>Most abundant mass denotes the mass of the molecular ion peak group calculated from natural isotopes abundance.

<sup>5</sup>Average mass, calculated from the average masses of the elements, weighted for abundance, i.e., the “centroid” of the distribution.

<sup>6</sup>Centroid cluster is the term used by Yergey and denotes the isotopic peaks group forming the cluster.

<sup>7</sup>Isotopic element is the element which occur in two or more natural isotopes.

<sup>8</sup>Agglomerate = aggregate.

atoms in the agglomerates described are higher than those commonly observed in compounds and have been chosen for proper illustration of the problem considered.

It is useful to determine the location  $m/z$  of the most intense peak of the "centroid" cluster which denotes the location of the most abundant peak of an isotopometric cluster (LAPIC). If the pattern contains  $k$  peaks with intensities  $P_i$ , the LAPIC is equal to the  $m/z$  value attributed to the main peak of the pattern:

$$\text{LAPIC} = (m_i/z) \quad \text{when} \quad \mathbf{P}_i = \mathbf{max} \quad \text{in range } i = 1 \div k$$

The upper numeric row shows locations ( $m/z$ ) of the main peaks (LAPIC) of single atom clusters, and the lower numeric row contains the number of atoms in the agglomerates and the LAPIC values for element aggregates.

The simple atom cluster and the aggregate pattern are substantially different. The LAPIC values of a single atom of isotopic elements are not pertinent for prediction of this parameter for the corresponding agglomerate, e.g., the value expected for  $S_{50}$  is 1,600, but the occurrence of natural isotopes results in the LAPIC increasing to 1,604, a difference of four mass units. The comparison of main peak locations of centroids (from both numeric rows of Fig. 1) shows that:

$$\mathbf{B}_{50} \neq 50 \bullet \mathbf{B}, \quad \mathbf{Br}_{20} \neq 20 \bullet \mathbf{Br}, \quad \mathbf{C}_{500} \neq 500 \bullet \mathbf{C}, \\ \mathbf{Cl}_{20} \neq 20 \bullet \mathbf{Cl}, \quad \mathbf{S}_{50} \neq 50 \bullet \mathbf{S} \quad \text{and} \quad \mathbf{Si}_{50} \neq 50 \bullet \mathbf{Si}$$

The location of the centroid's main peak is shifted a few units from the expected positions to higher  $m/z$  values. The values of observed shifts for the aggregates are:

- -10 for boron, +20 for bromine, +5 for carbon, +10 for chlorine,
- +4 for sulfur and +5 for silicon.

The location (LAPIC) of the main peak is the important parameter for prediction of the element formula of the (molecular or fragment) ion investigated. The forms of isotopomeric profiles for single atoms and the agglomerate are evidently different. Such facts are well known and have been described in the literature [7, 9, 11]. Figure 1 helps to explain the idea of the LAPIC parameter and gives a graphic representation of isotopomeric species that characterize element aggregates.

A simple pattern consisting of a few peaks only is transformed into a centroid created from many signals, generally resembling the Gauss curve. It may be seen that the isotopomeric clusters of all elements become normal distributions. This is especially evident for boron and bromine. Such trends are also found for the other elements considered, but the distributions observed are not symmetric. The isotopomeric cluster of the sulfur agglomerate is formed from two overlapping components, with peaks of the larger component shifted by one  $u$  compared to the smaller one. The clusters of bromine and chlorine aggregates are characteristic, as each second position (for odd  $n$ — $\text{Br}_{10}$ ,  $\text{Cl}_8$ , etc.—only odd  $m/z$

values) in such clusters is filled with a peak. The pictorial forms of isotopomeric pattern of the aggregates (in lower graphic row of the Table 1) may be used for fast and simple determination of the numbers of corresponding element atoms, which can be done by an experienced spectroscopist.

The forms of the isotopic element aggregates cannot be obtained by a simple multiplication of single atom species.

$$(\text{Elem})_i \neq i \cdot \text{Elem} \\ \text{property of aggregate} \neq \text{number of element} \cdot \text{property of element}$$

In these cases the prediction requires complex calculations based on probability rules. The knowledge of element agglomerates species may be significant for subsequent interpretation of, e.g., mass spectra. The problem described can be a source of significant errors in the determination of both molecular mass and summary formula of an investigated compound.

### Features of the LAPIC for element aggregates

The predictions for isotopic elements occurring in organic compounds are with carbon as an example presented. The scale of the  $(C)_n$  aggregates problem has been increasing in the course of polymer investigations. The calculations of isotopomeric cluster have been performed point-by-point for each aggregate in the range from  $n = 1$  up to  $n = 1,000$ . The LAPICs were calculated for all  $n$  values. The predictions show the following relation:

$$\text{LAPIC}_{C_n} \neq \text{LAPIC}_{C_l}, \quad \text{when } n > 92.$$

The function LAPIC vs  $n$  is an increasing function and some existing perturbations are hard to determine from graphs.

An improved presentation of the relations investigated is the  $\Delta$  LAPIC, the parameter describing the difference between two LAPICs corresponding to the two adjacent aggregates:

$$\Delta \text{LAPIC}_{C_n} = \text{LAPIC}_n - \text{LAPIC}_{(n-1)} \quad (2)$$

e.g., for aggregates  $C_{811}$ — $C_{810}$ .

In the full range of  $n$  considered the  $\Delta$  LAPIC value tends to remain constant ( $\Delta$  LAPIC = 12), except for 11 points (out of 1,000). The irregularities, corresponding to  $\Delta$  LAPIC = 13, are found for the following  $n$  values: 90, 181, 272, 363, 454, 545, 636, 727, 818, 909 and 1000. These values form an arithmetic sequence with the first term  $a_1 = 90$  and difference  $q = 91$ , so LAPIC<sub>C</sub> values in the range  $n$  from 1 up to 1,000 can be described by Eq. 3:

$$\text{LAPIC}_C = 12 \cdot n + \text{INT} \left( n + \frac{1}{91} \right) \quad (3)$$

The formula contains two parts; the first one related to mono-isotopic calculation and the second one the isotopomeric correction factor (ICF):

$$\text{LAPIC}_C = 12 \cdot n + \text{ICF}_C \quad (4)$$

The aggregates of other elements fundamental for organic compounds were calculated by such a method. The  $\Delta$  LAPIC values and possible equations for LAPIC predictions for isotopic elements forming organic compounds are summarized in Fig. 2.

Elements that form classic organic compounds and have natural isotopes were selected for consideration. Thanks to the known isotopic abundances, the LAPIC value can be easily predicted for the aggregates of:

- boron (up to  $\text{B}_{100}$ , values 10 and 11 u),
- bromine (up to  $\text{Br}_{20}$ , values 79 and 81 u),
- carbon (up to  $\text{C}_{1000}$ , values 12 and 13 u),
- chlorine (up to  $\text{Cl}_{20}$ , values 35 and 37 u),
- sulfur (up to  $\text{S}_{100}$ , values 32, 33 and 34 u) and
- silicon (up to  $\text{Si}_{100}$ , values 28, 29 and 30 u).

One element is described in each cell of Fig. 2. The numbers of element atoms in the aggregates presented Fig. 2 are chosen to cover ranges occurring commonly (excluding carbon, for which aggregates larger than  $\text{C}_{1000}$  occur in polymers) in medium- and high-mass organic compounds.

The graphs present the mass differences  $\Delta$  LAPIC vs atom number  $n$  in the aggregate, i.e.,  $\Delta \text{LAPIC} = (fn)$ . Such functions for most of the elements considered (excluding Br) are usually described as a line  $\Delta \text{LAPIC} = \text{const.}$ , with different  $\Delta$  LAPIC values for a few points  $n$ . These points are summarized below the graphs. Bromine is a special case. The graph of the function  $\Delta \text{LAPIC} = (fn)$  is saw-like, the higher (81) and lower (79) values of  $\Delta$  LAPIC are interlaced and none of them is the average atomic mass.

The proper equations (Eqs. 5, 6, 7, 8, 9, 10, 11 and 12) are summarized at the bottom of each cell. The natural isotope abundances of nitrogen and oxygen account for the differences observed at very high number atoms in the aggregate, and the existence of a single  $\Delta$  LAPIC value is found. These elements may be regarded as mono-isotopic. The  $\Delta$  LAPIC irregularities are observed

at high  $n$  values ( $n_N = 273$  and  $n_O = 451$ , respectively), which rarely occur in the actual compounds investigated, for these  $n$  the graphs are not shown.

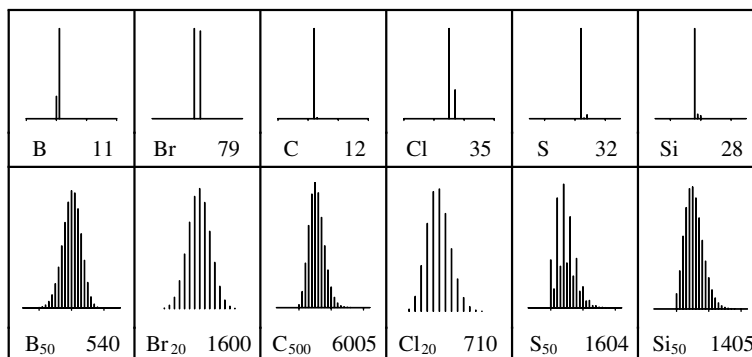
All the examples described show some regularity of the isotopomeric correction factor ( $\text{ICF}_e$ ), except for silicon. The  $n$  values connected with the disturbances for boron, bromine, carbon, chlorine and sulfur all form arithmetic sequences.

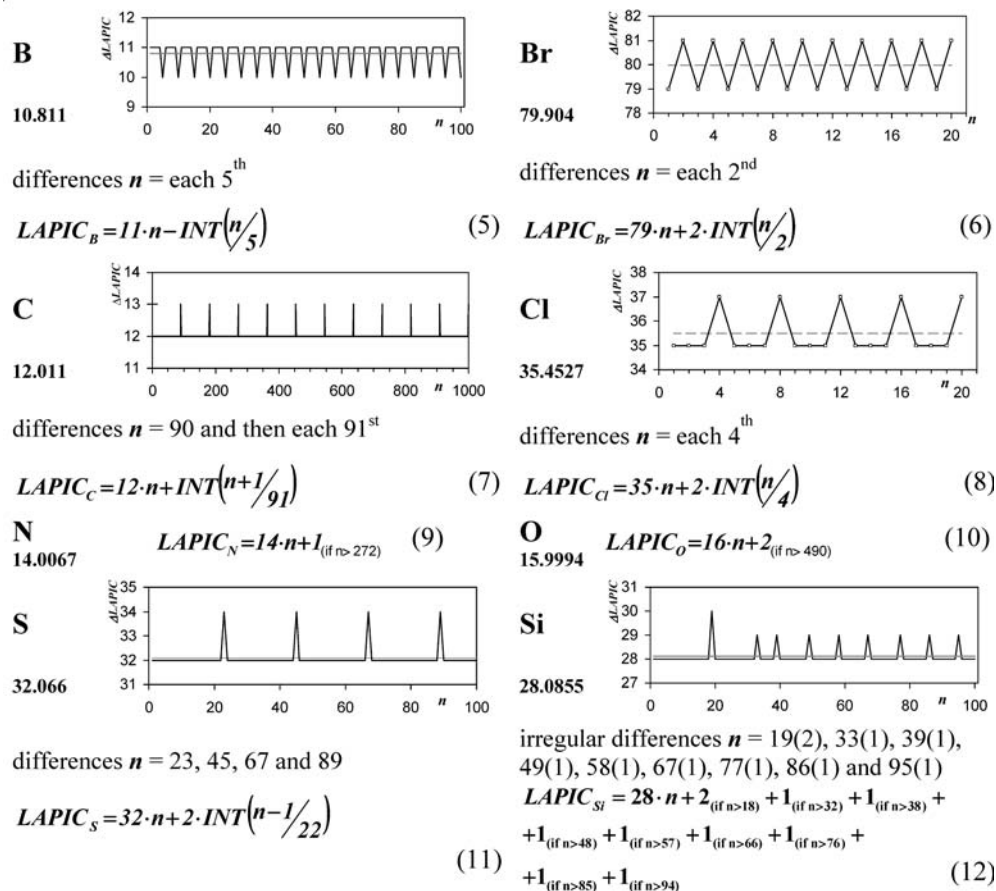
Bromine occurrence generates the highest differences. Each second atom of the element displaces the main peak of the cluster by two units toward a higher value of  $m/z$ . Each fourth occurrence of a chlorine atom generates a difference equal 2 up and each fifth occurrence of boron results in shifting one unit down. The aggregates containing sulfur and silicon result in differences over  $\text{S}_{22}$  and over  $\text{Si}_{18}$ . The changes observed for silicon are irregular, unlike those for all other elements considered. Carbon generates small shifts of the most abundant isotopomeric peak, but the number of carbon atoms in molecules, e.g., natural and synthetic polymers, creates important problems which should be solved by multi-isotopomeric analysis. The occurrence of these elements in a molecule of the compound investigated leads to the necessity of application of multi-isotopomeric techniques.

The combination of nitrogen and/or oxygen aggregates with any other elements is simple to predict, so both these elements can be regarded as mono-isotopic. The  $\Delta$  LAPICs occurring for silicon (up to  $\text{Si}_{100}$ ) are located irregularly and different values (28, 29 and 30) are observed, leading to a relatively complicated solution of  $\text{LAPIC}_{\text{Si}}$  prediction. The prediction of LAPIC is not disturbed by the occurrence of mono-isotopic elements, such as hydrogen, iodine, fluorine, phosphorus, etc. Beynon explained in detail the form of the molecular cluster containing some aggregates ( $\text{Br}_m\text{Cl}_n$ ) of bromine and/or chlorine (up to eight atoms of each halogen) [7].

In this investigation, the LAPIC values are calculated for all combinations of  $\text{Br}_m$  and  $\text{Cl}_n$  aggregates ( $m = 0-20$  and/or  $n = 0-20$ ) and the results are summarized in Table 1. The combinations of bromine and chlorine described in Table 1 appear to be sufficient for mass predictions of many compounds. In spite of the difficulties, the adducts of chlorine and bromine aggregates can be calculated from

**Fig. 1** Transformation of isotopic clusters of single atoms [5] in centroidal isotopomeric clusters of element aggregates





**Fig. 2** Differences of the most abundant peak location ( $\Delta L_{APIC} = fn$ ) as the isotopometric consequences on  $(\text{Elem})_n$  element aggregates observed in classic organic compounds

$$LAPIC_{Br+Cl} = 79 \cdot n_{Br} + 35 \cdot n_{Cl} + 2 \cdot \text{INT}\left(\frac{n_{Br}}{2} + \frac{n_{Cl}}{4}\right) \quad (13)$$

when  $n_{Br} = 0-20$  and  $n_{Cl} = 0, 2, 4, 6, 8, 10-20$ .

Nevertheless, some polychloro-polymers, e.g., PCV, require a special treatment due to the difficult problem of the simultaneous occurrence of a large number of carbons as well as numerous chlorine atoms in the high-mass molecule.

## Conclusions

Medium- and high-mass organic compounds show significant differences between experimental and expected ionic molecular patterns. Such problems are caused by isotopic species of the elements forming this ion and they influence the cluster form as well as the location of the main peak of the pattern considered. The shifting of the main peak of the ionic cluster can be the source of errors in molecular weight prediction for some organic compounds. The solution of this

problem is based on the treatment of the compound formula as an adduct of mono-element aggregates, which are analyzed separately and for which the  $L_{APIC}$  values can be calculated:

$$LAPIC_e = m_d \cdot n_e + ICF_e, \quad (14)$$

in which  $m_d$  denotes mass of dominated (or single) isotope (for Br  $m_d = 79$  u) and  $n_e$  is the number of element atoms in the agglomerate considered.

The correct value is composed of two parts: the component containing mono-isotopic element aggregates ( $m_{d \cdot n_e}$ ) and the  $ICF_e$ : elements such as hydrogen, iodine, fluorine and phosphorus are mono-isotopic (e.g.,  $ICF = 0$ ). Nitrogen and oxygen can be effectively treated as mono-isotopic ( $ICF = 0$ ). The  $ICF_e$  values of aggregates for other isotopomeric elements can be determined from the following relations:

$$\mathbf{B} \quad ICF_B = -\text{INT}\left(\frac{n}{5}\right) \quad (15)$$

$$\mathbf{Br} \quad ICF_{Br} = 2 \times \text{INT}\left(\frac{n}{2}\right) \quad (16)$$

$$\mathbf{C} \quad ICF_C = \text{INT}\left(n + \frac{1}{91}\right) \quad (17)$$

$$\mathbf{Cl} \quad ICF_{Cl} = 2 \times \text{INT}\left(\frac{n}{4}\right) \quad (18)$$



**Table 1** The locations of the most abundant peaks of isotopomeric clusters (LAPIC) calculated by MMIP of the Br<sub>m</sub>Cl<sub>n</sub> aggregates

Br	Cl										
	–	Cl	Cl <sub>2</sub>	Cl <sub>3</sub>	Cl <sub>4</sub>	Cl <sub>5</sub>	Cl <sub>6</sub>	Cl <sub>7</sub>	Cl <sub>8</sub>	Cl <sub>9</sub>	Cl <sub>10</sub>
–	0	35	70	105	142	177	212	247	284	319	354
Br	79	116	151	186	221	258	293	328	363	398	435
Br <sub>2</sub>	160	195	230	267	302	337	372	407	444	479	514
Br <sub>3</sub>	239	276	311	346	381	418	453	488	523	558	595
Br <sub>4</sub>	320	355	390	427	462	497	532	569	604	639	674
Br <sub>5</sub>	399	436	471	506	541	578	613	648	683	718	755
Br <sub>6</sub>	480	515	550	587	622	657	692	729	764	799	834
Br <sub>7</sub>	559	596	631	666	701	738	773	808	843	880	915
Br <sub>8</sub>	640	675	710	747	782	817	852	889	924	959	994
Br <sub>9</sub>	719	756	791	826	861	898	933	968	1,003	1,040	1,075
Br <sub>10</sub>	800	835	870	907	942	977	1,012	1,049	1,084	1,119	1,154
Br <sub>11</sub>	879	916	951	986	1,021	1,058	1,093	1,128	1,163	1,200	1,235
Br <sub>12</sub>	960	995	1,030	1,067	1,102	1,137	1,172	1,209	1,244	1,279	1,314
Br <sub>13</sub>	1,039	1,076	1,111	1,146	1,181	1,218	1,253	1,288	1,323	1,360	1,395
Br <sub>14</sub>	1,120	1,155	1,190	1,227	1,262	1,297	1,332	1,369	1,404	1,439	1,474
Br <sub>15</sub>	1,199	1,236	1,271	1,306	1,341	1,378	1,413	1,448	1,483	1,518	1,555
Br <sub>16</sub>	1,280	1,315	1,350	1,387	1,422	1,457	1,492	1,529	1,564	1,599	1,634
Br <sub>17</sub>	1,359	1,396	1,431	1,466	1,501	1,538	1,573	1,608	1,643	1,678	1,715
Br <sub>18</sub>	1,440	1,475	1,510	1,547	1,582	1,617	1,652	1,689	1,724	1,759	1,794
Br <sub>19</sub>	1,519	1,556	1,591	1,626	1,661	1,698	1,733	1,768	1,803	1,838	1,875
Br <sub>20</sub>	1,600	1,635	1,670	1,707	1,742	1,777	1,812	1,849	1,884	1,919	1,954

Br	Cl									
	Cl <sub>11</sub>	Cl <sub>12</sub>	Cl <sub>13</sub>	Cl <sub>14</sub>	Cl <sub>15</sub>	Cl <sub>16</sub>	Cl <sub>17</sub>	Cl <sub>18</sub>	Cl <sub>19</sub>	Cl <sub>20</sub>
–	389	426	461	496	531	568	603	638	673	710
Br	470	505	540	577	612	647	682	719	754	789
Br <sub>2</sub>	549	586	621	656	691	728	763	798	833	870
Br <sub>3</sub>	630	665	700	737	772	807	842	879	914	949
Br <sub>4</sub>	709	746	781	816	851	888	923	958	993	1,030
Br <sub>5</sub>	790	825	860	897	932	967	1,002	1,039	1,074	1,109
Br <sub>6</sub>	869	906	941	976	1,011	1,048	1,083	1,118	1,153	1,190
Br <sub>7</sub>	950	985	1,020	1,057	1,092	1,127	1,162	1,199	1,234	1,269
Br <sub>8</sub>	1,029	1,066	1,101	1,136	1,171	1,208	1,243	1,278	1,313	1,350
Br <sub>9</sub>	1,110	1,145	1,180	1,217	1,252	1,287	1,322	1,359	1,394	1,429
Br <sub>10</sub>	1,189	1,226	1,261	1,296	1,331	1,368	1,403	1,438	1,473	1,510
Br <sub>11</sub>	1,270	1,305	1,340	1,377	1,412	1,447	1,482	1,519	1,554	1,589
Br <sub>12</sub>	1,349	1,386	1,421	1,456	1,491	1,528	1,563	1,598	1,633	1,670
Br <sub>13</sub>	1,430	1,465	1,500	1,537	1,572	1,607	1,642	1,679	1,714	1,749
Br <sub>14</sub>	1,509	1,546	1,581	1,616	1,651	1,688	1,723	1,758	1,793	1,830
Br <sub>15</sub>	1,590	1,625	1,660	1,697	1,732	1,767	1,802	1,839	1,874	1,909
Br <sub>16</sub>	1,669	1,706	1,741	1,776	1,811	1,848	1,883	1,918	1,953	1,990
Br <sub>17</sub>	1,750	1,785	1,820	1,857	1,892	1,927	1,962	1,999	2,034	2,069
Br <sub>18</sub>	1,829	1,866	1,901	1,936	1,971	2,008	2,043	2,078	2,113	2,150
Br <sub>19</sub>	1,910	1,945	1,980	2,017	2,052	2,087	2,122	2,159	2,194	2,229
Br <sub>20</sub>	1,989	2,026	2,061	2,096	2,131	2,168	2,203	2,238	2,273	2,310

$$S \quad ICF_S = 2 \times \text{INT} \left( n - \frac{1}{22} \right) \quad (19)$$

$$SiICF_{Si} = 2_{(ifn>18)} + 1_{(ifn>32)} + \\ + 1_{(ifn>38)} + 1_{(ifn>48)} + 1_{(ifn>57)} + \\ + 1_{(ifn>66)} + 1_{(ifn>76)} + 1_{(ifn>85)} + 1_{(ifn>94)} \quad (20)$$

The factor for most combinations of the bromine and chlorine can be predicted from Eq. 21:

$$Br+Cl \quad ICF_{Br+Cl} = 2 \times \text{INT} \left( \frac{n_{Br}}{2} + \frac{n_{Cl}}{4} \right) \quad (21)$$

The solution presented is a simple aid that can be applied successfully for most organic compounds. A knowledge of the rules forming the cluster of the aggregate can be important for a correct interpretation of this cluster. The comparison of LAPIC (main peak location) of the cluster and the mass of the ion considered can provide a substitute for the much more complex method of isotopomeric analysis applied in mass spectra interpretation [11, 12].

The value of the global parameter  $LAPIC_{\Sigma}$  is calculated by Eq. 22 and concerns the elements that usually form organic compounds:

$$LAPIC_{\Sigma} = \sum_{i=1}^k (m_{d_i} \cdot n_{e_i}) + ICF_{\Sigma}. \quad (22)$$

The first part concerns the mono-isotopic prediction from the dominant isomer of each element that occurs in the compound and  $ICF_{\Sigma}$  means the total isotopomeric correction factor. However, the factor depends on the element aggregates forming the compound, but the value cannot be treated as a simple adduct of the agglomerate parts:

$$ICF_{\Sigma} \neq \sum ICF_e.$$

The method described is not recommended for bromo/chloro derivatives of the silanes, for which each composition of these isotopic elements must be calculated separately. The relations are very complex for compounds containing three or more isotopic elements and in such cases polynomial calculations based on probability rules should be applied (e.g. [11–13]). The problem presented can be important in molecular weight prediction of medium and high-mass organic compounds. The comparison of  $LAPIC$  with the element formula can be an effective help, e.g., in mass-spectra interpretation since the prediction of  $LAPIC$  allows the correct connection of the main peak of the ion investigated with the expected ion formula. The solution presented can also be applied to investigation of mass spectra of medium- and high-mass organic compounds

characterized by the occurrence of elements “classic” for organic compounds.

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