

Diophantine Approach to Isotopic Abundance Calculations

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Polynomial approaches have been used in the literature for calculating the isotopic abundance of a given formula containing polyisotopic elements. These approaches limit the number of elements in the formula being calculated. A more general and flexible computer program based on a Diophantine algorithm has been developed. The equation used for calculating the fractional abundance is converted into a logarithmic form to avoid the use of a Gamma function, which limits the number of occurrences of an element one may calculate by a computer program. To reduce computation time and error for heavy isotopic clusters, a method similar to that described by Yergey is used. In the program, the formula weight is defined and calculated. The mass assignment of the isotopic cluster is corrected for the mass defect of the elements so that the calculated output can be directly compared with low-resolution mass spectrometric measurements. This program is written in FORTRAN V for use on a Data General Eclipse C/350 computer. It is capable of handling all of the elements, from hydrogen to uranium, with stable, naturally occurring isotopes. The program is useful for identification or confirmation of organometallics and coordination compounds, as well as for middle-mass and polymeric materials whose mass spectra contain complex isotopic patterns.

Mass spectrometry was originally used by physicists as a convenient and effective way to detect isotopes. It was later developed to analyze organic materials and volatile organometallics. When these materials contain elements with multiple isotopes, their mass spectra can be very complex.

With the improvements in mass spectrometric instrumentation, ions in the "middle-mass" range (1000-10000 amu) can be detected (1). In these middle-mass ions, the number of occurrences of each element is usually large. Low abundance isotopes, which do not play a significant role in low-mass ions, can make significant contributions to the mass spectral pattern as their number of occurrences increases. For example, ^{13}C contributes only 1.1% relative to ^{12}C in nature. In the styrene molecular ion, C_8H_8 , the most abundant isotopic peak is at m/z 104 and contains only ^{12}C atoms. The abundance of the C_8H_8 ion containing one ^{13}C atom is 8.8% relative to the most abundant isotopic peak. However, for polystyrene with a degree of polymerization of 100 ($\text{C}_{804}\text{H}_{810}$), the isotopic peak containing one ^{13}C atom is about nine times as abundant as the isotopic peak containing only ^{12}C atoms. The most abundant ionic species in the molecular ion cluster has a formula $^{12}\text{C}_{795}^{13}\text{C}_9\text{H}_{810}$ (1, 2). Therefore, complex isotopic distributions are also observed in middle-mass and heavy ions (3).

Precise masses of different isotopic combinations are all different. For those isotopic combinations with the same nominal mass, the mass spread is often less than 50 ppm (4). Middle-mass and heavy ions, especially, often require ultrahigh resolution (>100 000) to resolve the peaks corresponding to individual isotopic combinations (5). Identification of the isotopic composition by high-resolution mass spectrometry

is, therefore, impractical. Isotopic clusters are usually identified by low-resolution mass spectrometric measurements. An isotopic peak is actually the overall unresolved isotopic combinations appearing at a particular nominal mass.

To identify complex isotopic clusters obtained from low-resolution mass spectrometric measurements, the theoretical isotopic distributions of the molecules or fragments are needed for comparisons. Calculations of isotopic abundance are usually long and tedious, almost always requiring a computer program. Several computer programs for these isotopic abundance calculations are available in the literature (4, 6-12), but most of them have only narrow capability. The number of occurrences of each element or the number of elements is usually limited. Furthermore, the mass defects of the elements are not considered in these calculations. In middle-mass ion clusters, the measured mass of an isotopic peak can be significantly different from the sum of the nominal masses of the isotopes. This discrepancy results when the mass defects of the elements are not considered.

Because of the wide range in mass in many isotopic clusters, it would be convenient to use formula weight, a single nominal mass, to describe the clusters. In this paper, the formula weight is defined as the sum of the products of the nominal mass of the most abundant isotope times the number of occurrences of that element in the molecule or fragment (13) corrected by the mass defects. This formula weight is not necessarily the same as the nominal mass of either the most abundant or the lightest isotopic peak in the cluster.

A computer program has been developed to handle all of the elements, from hydrogen to uranium, that have stable, naturally occurring isotopes. The program calculates the isotopic distribution of a given formula, defines the formula weight, and corrects the nominal mass by considering mass defects. There are no limits on mass number, number of elements, or the number of occurrences of each element. The program is written in FORTRAN V for use on a Data General Eclipse C/350 computer.

DIOPHANTINE APPROACH TO ISOTOPIC-ABUNDANCE CALCULATIONS

The only input needed by the computer program is the chemical formula of a molecule or a fragment. Other information needed for the calculations (the mass of the lightest isotope, the number of isotopes, the natural abundances of all the isotopes, and the mass defects for all the elements) is stored in the DATA blocks of the program. The number of isotopes is defined as one plus the difference in masses of the heaviest and the lightest isotopes of the element. This includes some isotopes that do not actually occur in nature, with their fractional abundances set to zero. The values of the natural abundances of the isotopes are taken from ref 14.

Mathematically, isotopic abundance calculations involve probability theory and combinatorial analysis. Methods of calculation can be found in several references (15-17). All of them use polynomial approaches to find isotopic distributions among elements in a given formula, but they limit the number of elements in the formula being calculated. For each additional element, an additional factor $(x_1 + x_2 + \dots)$, where x_1, x_2, \dots represent the isotopes of the element x , is needed

Chart I

m_1	m_2	m_3
2	0	0
1	1	0
1	0	1
0	2	0
0	1	1
0	0	2

for polynomial expansion and collection of terms (12). In the early 1970s, a different approach was developed to provide simplicity and flexibility to the calculations (18); in this approach, a Diophantine equation was used to calculate all of the possible isotopic combinations of a given element. The isotopic distribution of each element in a given formula was then convoluted to give the fractional abundance of the isotope cluster. However, no details of this approach were published.

Diophantine equations can be defined generally as a set of algebraic equations with integer coefficients for which integer solutions are desired (19). The number of solutions to a specific form of Diophantine equation varies depending on the values of parameters (other than the variables) in the equation. A Diophantine restraint equation can be expressed by

$$\sum_{i=1}^k m_i = n \quad (1)$$

where n is the number of atoms (occurrences) of each element in a formula, k is the number of isotopes of that element, and m_i is the number of occurrences of the i th isotope of the element.

In the computer program we describe here, the number of isotopes is determined on a continuous mass basis. For example, chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl . In the program, the number of isotopes for chlorine is defined as 3 ($k = 37 - 35 + 1$).

All of the possible isotopic combinations for a chlorine molecule are represented by the Diophantine output shown in Chart I, where m_1 represents ^{35}Cl , m_2 represents ^{36}Cl , and m_3 represents ^{37}Cl . A total of six combinations is found.

Searching for these isotopic combinations by computer is not straightforward. Figure 1 is a flow chart of the Diophantine subroutine, in which L counts the number of isotopic combinations of an element being calculated, and $K1$ and $K2$ are the control parameters. N and NI are the number of occurrences (atoms) and the number of isotopes, respectively, of the element. $M(I)$ is the number of occurrences of the I th isotope, where $I = 1, 2, \dots, NI$. In Figure 1, the $M(I)$ values are printed after completion of each search. The isotopic calculation program does not print the $M(I)$ values, but proceeds with the abundance calculations for each combination.

For each combination of the isotopes for a given element, the fractional abundance can be calculated by the following equation:

$$F_i = \frac{n!}{m_1! m_2! \dots m_n!} f_1^{m_1} f_2^{m_2} \dots f_n^{m_n} \\ = \frac{n!}{\prod_{j=1}^k m_j!} \prod_{j=1}^k (f_j)^{m_j} \quad (2)$$

where F_i is the fractional abundance of the i th combination, f_j is the fractional abundance of the j th isotope, and n , k , and m_j are defined as in eq 1.

The factorials can be evaluated by using the Gamma function library program, which is stored in the computer. The largest factorial which the Data General Eclipse C/350 computer can evaluate is $\Gamma(58) = 57! = 4.05 \times 10^{76}$. Above

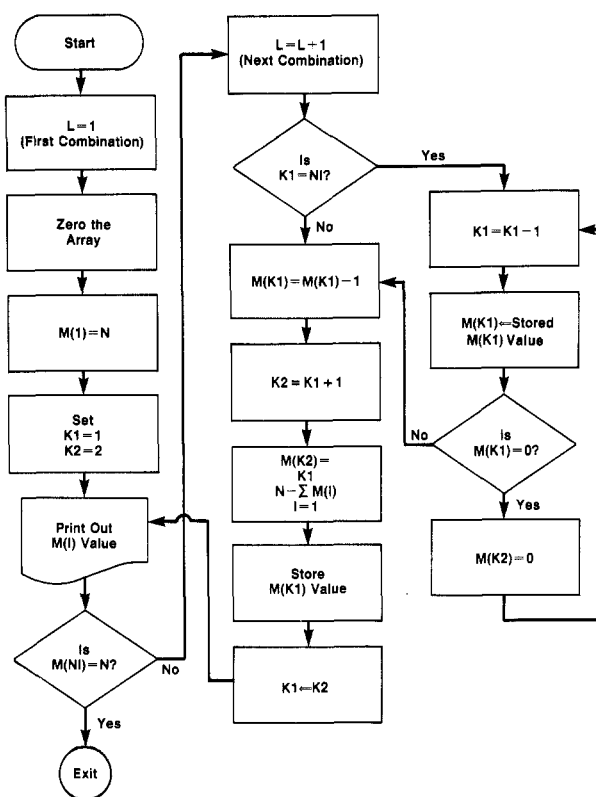


Figure 1. Flow chart of the Diophantine subroutine.

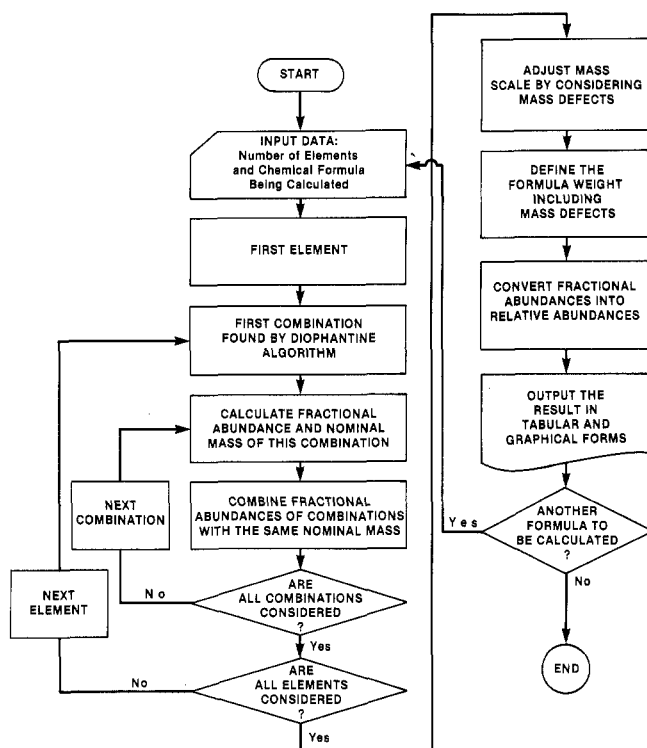


Figure 2. Algorithm of the isotopic abundance convolution program.

this, the computer will "overflow". This limits the maximum number of occurrences for an element to 57. To overcome this limitation, eq 1 is converted into a more generally useful logarithmic form

$$\log F_i = \sum_{\sigma=1}^n \log \sigma - \sum_{j=1}^k [\sum_{i=1}^{m_j} \log i] + \sum_{j=1}^k [m_j \log f_j] \quad (3)$$

The nominal mass of this combination is also calculated. Calculations of the fractional abundances and nominal masses are repeated for all of the other combinations. The fractional

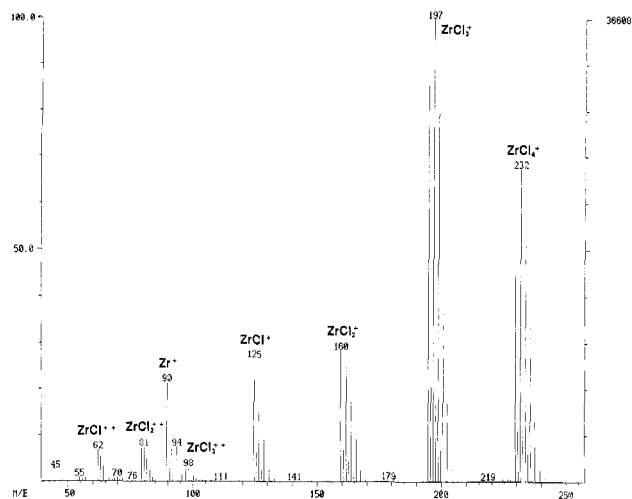


Figure 3. 70-eV electron-impact ionization mass spectrum of zirconium chloride subjected to direct-insertion probe analysis.

abundances of the same nominal masses are summed. After all of the possible combinations are considered, an isotopic distribution for that element results. The procedure is repeated for the other elements and, finally, the fractional abundances of all the nominal masses in the cluster of the given formula are obtained. This is a convoluted mass spectrum of the given formula.

The mass assignments and the formula weight are then corrected by considering the mass defects of all of the elements in the calculations. Since the mass defects of the isotopes for a given element do not differ significantly (14), only the mass defect of the most abundant isotope of each element is considered.

Finally, fractional abundances are converted into relative abundances. The results of the isotopic abundance convolution are presented in both tabular and graphical (bar plot) forms, and the formula weight is included.

Figure 2 shows the algorithm of the isotopic abundance convolution program run interactively on a Data General Eclipse C/350 computer. The chemical formula was input via a Data General Dasher D200 terminal in a repetitive A2,I3 format. The I3 format is adequate to calculate any isotopic distribution for the clusters measurable by current mass spectrometers. Copies of the listing are available from the author.

CALCULATION OF FRACTIONAL ABUNDANCES FOR LARGE ISOTOPIC CLUSTERS

For calculating the fractional abundances of a large isotopic cluster, the straightforward logarithmic approach becomes inefficient, because both computation time and error increase due to numerous repetitive calculations.

Let us assume that a given formula contains 500 atoms of an element with two isotopes. The first three isotopic combinations obtained by eq 1 are

m_1 (isotope 1)	m_2 (isotope 2)
500	0
499	1
498	2

With the direct logarithmic approach, there are more than 2000 computer manipulations (call subroutine for logarithm, additions, subtractions, and multiplications) for EACH combination. Thus, more than 6000 calculations are required for these three combinations.

The number of calculations can be reduced substantially if we use the ratio of two consecutive combinations, a method

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THE CONVOLUTED MASS SPECTRUM FOR ZR 1CL 3

M/Z  F.A.  R.A.
195  .22386  77.41
196  .04885  16.89
197  .28918  100.00
198  .04686  16.21
199  .21577  74.61
200  .01499  5.18
201  .11495  39.75
202  .00160  .55
203  .03734  12.91
204  .00000  .00
205  .00621  2.15
206  .00000  .00
207  .00040  .14

SUM = 1.00000  345.90

*** THE FORMULA WEIGHT IS 195 ***

THE CONVOLUTED MASS SPECTRUM FOR ZR 1CL 4

M/Z  F.A.  R.A.
230  .16962  52.05
231  .03702  13.54
232  .27335  100.00
233  .04735  17.32
234  .23355  65.44
235  .02271  8.31
236  .13937  50.99
237  .00464  1.77
238  .05614  20.54
239  .00039  .14
240  .01375  5.03
241  .00000  .00
242  .00181  .55
243  .00000  .00
244  .00010  .04

SUM = 1.00000  365.63

*** THE FORMULA WEIGHT IS 230 ***

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Figure 4. Computer outputs of the calculated isotopic patterns for $ZrCl_3^+$ (left) and $ZrCl_4^+$ (right).

THE CONVOLUTED MASS SPECTRUM FOR C 24 H 20GE 1

M/Z	F.A.	R.A.
378	.15629	51.72
379	.04263	14.11
380	.21437	70.94
381	.11655	38.57
382	.30221	100.00
383	.07873	26.05
384	.06937	22.95
385	.01699	5.62
386	.00216	.72
387	.00018	.06
388	.00001	.00

SUM = .99950 330.73

*** THE FORMULA WEIGHT IS 382 ***

Figure 5. Calculated mass spectrum for the molecular ion of tetraphenylgermane.

THE CONVOLUTED MASS SPECTRUM FOR C 14 H 20 O 3MO 1GE 1

M/Z	F.A.	R.A.
398	.02753	18.28
399	.00444	2.95
400	.05310	35.26
401	.04620	30.68
402	.10589	70.32
403	.07552	50.15
404	.13979	92.83
405	.10328	68.59
406	.15059	100.00
407	.07864	52.22
408	.11814	78.45
409	.03097	20.57
410	.04945	32.84
411	.00773	5.13
412	.00719	4.77
413	.00109	.73
414	.00012	.08
415	.00001	.01
416	.00000	.00

SUM = .99970 663.86

*** THE FORMULA WEIGHT IS 408 ***

Figure 6. Calculated mass spectrum for the molecular ion of π -C₉H₅(CO)₃MoGe(C₂H₅)₃.

similar to that suggested by Yergey (20). For the i th combination, the fractional abundance is

$$F_i = \frac{n!}{\prod_{j=1}^k m_j!} \prod_{j=1}^k (f_j)^{m_j} = n! \prod_{j=1}^k \frac{(f_j)^{m_j}}{(m_j)!} \quad (4)$$

Similarly, the fractional abundance of the $(i+1)$ th combination is

$$F_{i+1} = n! \prod_{j=1}^k \frac{(f_j')^{m_j'}}{(m_j')!} \quad (5)$$

If we divide eq 5 by eq 4, we obtain

$$\frac{F_{i+1}}{F_i} = \prod_{j=1}^k \frac{(m_j)! (f_j')^{m_j'}}{(f_j)^{m_j} (m_j')!} = \prod_{j=1}^k \rho_j \quad (6)$$

where $\rho_j = [(m_j)! (f_j')^{m_j'}] / [(f_j)^{m_j} (m_j')!]$ and $f_j = f_j'$ for each isotope.

The value of ρ_j , where $j = 1, 2, \dots, k$, can be obtained by one of the following three equations, depending on the values of m_j and m_j' :

$$\rho_j = \frac{(m_j)(m_j-1) \dots (m_j'+1)}{(f_j)^{(m_j-m_j')}} \quad \text{if } m_j > m_j' \quad (7)$$

$$\rho_j = 1 \quad \text{if } m_j = m_j' \quad (8)$$

$$\rho_j = \frac{(f_j)^{(m_j-m_j')}}{(m_j')(m_j'-1) \dots (m_j+1)} \quad \text{if } m_j < m_j' \quad (9)$$

These equations can be converted to logarithmic forms as shown in eq 10-12, respectively.

$$\log \rho_j = \sum_{\sigma=m_j'+1}^{m_j} \log \sigma - (m_j - m_j') \log f_j \quad (10)$$

$$\log \rho_j = 0 \quad (11)$$

$$\log \rho_j = (m_j' - m_j) \log f_j - \sum_{\sigma=m_j+1}^{m_j'} \log \sigma \quad (12)$$

For any isotopic combination with $m_j = n$ for $j = \lambda$ and $m_j = 0$ for $j \neq \lambda$, where $\lambda = 1, 2, \dots, k$, the fractional abundance can be obtained by combining eq 4 with eq 1

$$F_i = f_\lambda^n$$

or

$$\log F_i = n \log f_\lambda \quad (13)$$

With this modified approach, the total number of calculations for the first three combinations of $n = 500$ and $k = 2$ is reduced from more than 6000 to fewer than 25, thereby reducing both computation time and error.

APPLICATIONS

One of the uses of this computer program is to recognize the isotopic patterns of clusters containing polyisotopic elements. Usually, a complete formula of the molecule or fragment is not needed. For organic compounds, the most

THE CONVOLUTED MASS SPECTRUM FOR C 804 H 810

a

M/Z	F.A.	R.A.
10464	.00004	.08 !
10465	.00036	.77 !
10466	.00166	3.50 !***
10467	.00507	10.67 !*****
10468	.01156	24.34 !*****
10469	.02108	44.37 !*****
10470	.03198	67.31 !*****
10471	.04153	87.42 !*****
10472	.04714	99.23 !*****
10473	.04751	100.00 !*****
10474	.04303	90.59 !*****
10475	.03540	74.51 !*****
10476	.02665	56.11 !*****
10477	.01850	38.95 !*****
10478	.01191	25.08 !*****
10479	.00715	15.05 !*****
10480	.00402	8.46 !*****
10481	.00212	4.47 !***
10482	.00106	2.23 !**
10483	.00050	1.05 !*
10484	.00022	.47 !
10485	.00009	.20 !
10486	.00004	.08 !
10487	.00001	.03 !
10488	.00001	.01 !
10489	.00000	.00 !

SUM = .35867 754.97

*** THE FORMULA WEIGHT IS 10464 ***

THE CONVOLUTED MASS SPECTRUM FOR C 804 H 810

b

M/Z	F.A.	R.A.
10464	.00011	.08 !
10465	.00101	.77 !
10466	.00464	3.50 !***
10467	.01413	10.67 !*****
10468	.03224	24.34 !*****
10469	.05876	44.36 !*****
10470	.08915	67.31 !*****
10471	.11579	87.42 !*****
10472	.13143	99.23 !*****
10473	.13245	100.00 !*****
10474	.11998	90.59 !*****
10475	.09865	74.51 !*****
10476	.07431	56.11 !*****
10477	.05159	38.95 !*****
10478	.03322	25.08 !*****
10479	.01994	15.05 !*****
10480	.01121	8.46 !*****
10481	.00592	4.47 !***
10482	.00295	2.23 !**
10483	.00139	1.05 !*
10484	.00062	.47 !
10485	.00026	.20 !
10486	.00011	.08 !
10487	.00004	.03 !
10488	.00002	.01 !
10489	.00001	.00 !

SUM = .99997 754.97

*** THE FORMULA WEIGHT IS 10464 ***

Figure 7. Calculated isotopic pattern for a polystyrene oligomer ion, C₈₀₄H₈₁₀ (degree of polymerization = 100): (a) using eq 3; (b) using eq 10-13.

characteristic isotopic patterns are observed in the mass spectra of chlorine- and/or bromine-containing compounds. These patterns can be used to identify the distribution of chlorine/bromine in organic molecules because they are not significantly altered by the presence of other elements, such as carbon, hydrogen, oxygen, and nitrogen. Beynon has calculated the chlorine/bromine isotopic patterns for as many as eight halogen atoms (17). Similarly, for most organometallics the isotopic patterns can be recognized by determining the patterns produced by the polyisotopic transition metals that are present (4).

A typical comparison of experimental and calculated results is shown in Figures 3 and 4. Figure 3 is a 70-eV electron-impact-ionization mass spectrum of zirconium chloride acquired on a Finnigan 4000 mass spectrometer. The most significant ions in the spectrum are the clusters corresponding to ZrCl₃⁺ and ZrCl₄⁺. Figure 4 shows the calculated isotopic

patterns of these two clusters in both tabular and graphic forms. There is excellent agreement between the calculated and experimental isotopic patterns for these zirconium chloride species.

Formula weight, as defined in the introduction, is the sum of the products of the precise mass of the most abundant isotope times its occurrence in a given formula. It can be the same as the nominal mass of the lightest, most abundant, or any isotopic peak. As in most cases, the formula weights of the zirconium chloride ion clusters are the same as the nominal masses of the lightest isotopic peaks (195 amu for ZrCl₃⁺ and 230 amu for ZrCl₄⁺). For tetraphenylgermane (12), (C₆H₅)₄Ge, the formula weight is the same as the nominal mass of the most abundant isotopic peak (382 amu), as shown in Figure 5. In other cases, formula weight is not the same as the nominal mass of either the lightest or the most abundant isotopic peak, as shown in Figure 6 for π-C₅H₅(CO)₃MoGe-

(C_2H_5)₃ (408 amu) (4). When the formula weight is different from the nominal mass of the lightest isotopic peak, the isotopic peak corresponding to the formula weight is not monoisotopic (containing only one isotope contributed by each element).

To demonstrate the capabilities of this program in calculating "middle-mass" and heavy ion clusters, a theoretical isotopic pattern was calculated for a polystyrene oligomer with a degree of polymerization of 100, $C_{804}H_{810}$. Figure 7 shows the results of this calculation. If only the nominal masses of carbon and hydrogen are used, the formula weight is 10458 amu. When the mass defects of carbon and hydrogen are considered, the formula weight is 10464 amu. The most abundant isotopic peak in this oligomer ion cluster is found at 10473 amu, as pointed out by Matsuo et al. (2).

Figure 7 demonstrates the problems of using any polyisotopic material as a high-mass standard, for instance, polystyrene as suggested by Matsuo et al. Isotopic patterns in the mass spectra of these materials are extremely complex and may be distorted by mass spectrometric measurements. In the $C_{804}H_{810}$ ion cluster, the intensities of several isotopic peaks are so similar that the computer may select the wrong isotopic peak for mass calibration. The problem is similar in the mass spectra of several oligomer ion clusters of hydrocarbons or perfluorohydrocarbons with carbon numbers greater than 90, and it can become even more complicated if protonated or hydride-abstracted molecular ions are present.

The results in Figure 7a were obtained by using eq 3 for the abundance calculations. The fractional abundance at each nominal mass is the probability of finding all of the ionic species with the specific nominal mass in an isotopic cluster. The sum of all of the fractional abundances in an isotopic cluster should be unity. By use of the straightforward logarithmic method of eq 3, the total fractional abundance of the polystyrene cluster is 0.359 because of the loss of significance from numerous calculations. With the modified logarithmic method of eq 10–13, the total fractional abundance is 1.000, as shown in Figure 7b. However, the same relative abundances are obtained by either method. The computation time is reduced from 4.5 min for the straightforward logarithmic method to less than 25 s for the modified method.

CONCLUSION

This paper introduces a Diophantine approach for calculating distributions of stable, naturally occurring isotopes for

a given chemical formula by computer. The most obvious uses of the computer program described are for the mass spectral identification and confirmation of organometallics, coordination compounds, and middle-mass and polymeric materials. This program can be extended to the deconvolution of overlapped isotopic clusters, the analysis of isotopic labeling, and the calculations of isotopic distributions in various types of mass spectrometry/mass spectrometry (MS/MS) spectra (21).

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