

## Lab Documentation

# A Guided-Inquiry Exercise for Student Discovery of the Chlorine Rule and a Methodology for Use of the Rule in Structure Determinations

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## Abstract

Students participate in a guided-inquiry exercise and discover a stoichiometric relationship in the form of a chlorine rule that applies to ideal  $\text{Br}_m\text{Cl}_n$  compounds (i.e., those for which the effects of all isotopes except  $^{79}\text{Br}$  and  $^{81}\text{Br}$  in a 1:1 ratio and  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in a 3:1 ratio are ignored). Then students apply the chlorine rule to the analysis of the mass spectra of real  $\text{Br}_m\text{Cl}_n$  compounds. A  $\text{Br}_m\text{Cl}_n$  compound contains  $m$  bromine,  $n$  chlorine and any combination of C, H, O and N atoms in its formula. The latter elements are omitted from the generalized formula, because small numbers of them have been demonstrated to be insignificant with regard to the mass spectral determination of  $n$  and  $m$ . Students have successfully found the value of  $n$  and  $m$  for 68 of 69 compounds for which the sum of  $m$  and  $n$  is equal to or greater than two by the methodology presented. Formulas that exceed a single chlorine atom plus either one sulfur atom or one silicon atom pose the only significant problems to the method, owing to the  $^{34}\text{S}$  isotope of sulfur and the  $^{30}\text{Si}$  isotope of silicon. Tables are provided that show the mass spectra analyzed.

## Introduction<sup>1</sup>

This is a report of a four-phase study conducted to see if students could discover the chlorine rule by a guided inquiry, learn how to apply the chlorine rule by completing a self-paced tutorial, and apply the rule as a beginning step in structural problems (i.e., the identification of the number of chlorine and bromine atoms in an unknown's formula). A fourth phase was added to help validate the methodology presented. Four appendixes are included. They are a shorthand method for expanding binomials (Appendix 1), a discussion of the mass spectral effect of sulfur on the mass spectra of  $\text{Br}_m\text{Cl}_n\text{S}_q$  compounds (Appendix 2), a guide to aid in the correlation of  $A + 2$  clusters with structural features (Appendix 3), and a discussion of the mass spectral effects of  $^{13}\text{C}$  and  $^2\text{H}$  on the mass spectra of  $\text{Br}_m\text{Cl}_n$  compounds (Appendix 4). The supplemental material supports the findings in the accompanying paper.

In the first phase, the students work a series of problems, which taken collectively leads them to an empirical discovery of a chlorine rule for determining the number of chlorine atoms in a compound that contains

multiple atoms of chlorine and bromine. The number of bromine atoms is then determined. A certain amount of background information is provided to students to get them started. The exercise in Handout 1 was developed to allow students to discover the chlorine rule on their own by a guided-inquiry exercise.

All that is needed to implement the procedures discussed herein is a ruler marked off in millimeters. The 15-cm Fisher Scientific ruler, catalog number 09-016, was used by students to analyze mass spectra that were obtained from the Internet. No chemicals are required, and no chemical hazards or related safety issues are present.

### Derivation of the Chlorine Rule by a Guided-Inquiry Exercise (Handout 1)—Phase 1

Bromine exists as a pair of isotopes,  $^{79}\text{Br}$  and  $^{81}\text{Br}$ , in a near 1:1 ratio, and chlorine as  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in a near 3:1 ratio. When either or both of these atoms are present in a sample compound, the mass spectrum of the compound often reveals their presence by a set of molecular-ion peaks, two mass units apart. This set of peaks will be referred to as the molecular-ion cluster. For this discussion, only the peaks needed for the chlorine analysis are considered as cluster peaks. The relative intensities of cluster peaks can be found from peak heights in a mass spectrum or from tabulated relative abundance data. As a stoichiometric tool, a molecular-ion cluster is a set of relative intensity values that are normalized to the intensity of the cluster's highest-mass molecular ion, which is taken as unity. Consider the molecular-ion region of the mass spectrum of  $\text{CHBr}_1\text{Cl}_2$ , which is shown below as it is obtained from Yan's (*I*) computer program, which computes isotope patterns using the known isotope abundances of each element.

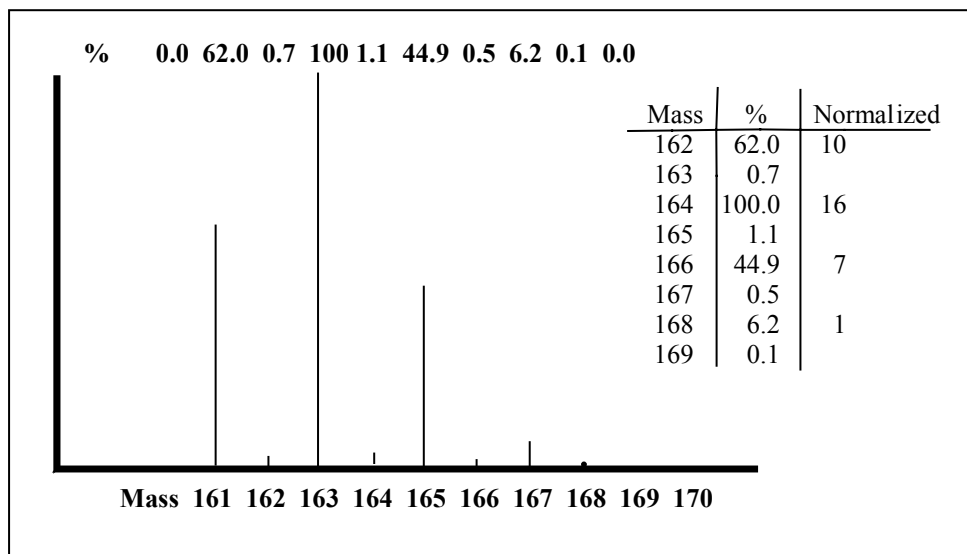


Figure 1. Computer-generated isotope pattern and table of relative abundances<sup>2</sup> for  $\text{CHBrCl}_2$ .

When the percentages 62.0, 100.0, 44.9, and 6.2 are divided by 6.2, the result is the normalized cluster 10:16:7:1. These four numbers are the intensities in a mass spectrum of the four molecular ions, two mass units

apart, starting with the lowest-mass molecular ion M of mass 162. The lowest-mass ion contains no  $^{81}\text{Br}$  or  $^{37}\text{Cl}$  isotopes only  $^{79}\text{Br}$  and  $^{35}\text{Cl}$ . The normalized intensity of this ion is 10, the first number in the cluster. Likewise, the highest-mass ion in the cluster contains no  $^{79}\text{Br}$  or  $^{35}\text{Cl}$  only  $^{81}\text{Br}$  and  $^{37}\text{Cl}$ . The normalized intensity of this ion is 1, the last number in the cluster. For reference, the number of peaks in a cluster is  $M$ , and the intensity of the leftmost cluster peak is L and the rightmost peak R. For  $\text{CHBrCl}_2$ ,  $M = 4$ ,  $L = 62.0$ ,  $R = 6.2$  and the ratio  $L/R = I_M$  (the normalized intensity of M); therefore,  $I_M = 62.0/6.2 = 10$ .

If  $m$  = the number of Br atoms and  $n$  = the number of Cl atoms, a real cluster is mimicked by the set of coefficients generated by expanding the binomial pair  $(a + b)^m(3a + b)^n$  (2). The binomial pair consists of a bromine binomial  $(a + b)^m$  and a chlorine binomial  $(3a + b)^n$ . In the bromine binomial,  $a$  represents  $^{79}\text{Br}$  and  $b$  represents  $^{81}\text{Br}$ ; the approximate 1:1 ratio of bromine isotopes is reflected in the coefficients of  $a$  and  $b$ . The 3:1 abundance ratio of  $^{35}\text{Cl}$  to  $^{37}\text{Cl}$  is reflected in the chlorine binomial. The binomial pair predicts the peak intensities of molecular-ion clusters of ideal  $\text{Br}_m\text{Cl}_n$  compounds (i.e., those in which only the isotopes of bromine and chlorine contribute to the molecular-ion cluster). The model-predicted peak intensities approximate actual intensities.

The expansion of the binomial pair for  $m = 1$  and  $n = 2$  gives the polynomial  $9a^3 + 15a^2b + 7ab^2 + 1b^3$ , and the coefficients give the ideal cluster 9:15:7:1; whereas, the cluster for  $\text{CHBr}_1\text{Cl}_2$ , a real  $\text{Br}_1\text{Cl}_2$  compound, is 10:16:7:1. If you wish to see these cluster values the way they appear in a mass spectrum, go to <http://www.ncsu.edu/labwrite/res/res-home.html> and follow the instructions for creating a histogram.<sup>3</sup> The expansion of the binomial pair always gives a cluster or isotope pattern for an ideal compound directly normalized to  $R = 1$ . The ratio of the leftmost to rightmost peak is 9:1 for the ideal  $\text{Br}_1\text{Cl}_2$  compound and 10:1 for the real compound. The expansion of the binomial pair for various values of  $m$  and  $n$  provides ideal clusters that are useful in the analysis of real compounds. Start with the first three problems.

**Problem 1:** Expand the binomial pair to find molecular-ion clusters for ideal  $\text{Br}_1$ ,  $\text{Br}_2$ ,  $\text{Br}_3$ ,  $\text{Cl}_1$ ,  $\text{Br}_1\text{Cl}_1$ ,  $\text{Br}_2\text{Cl}_1$ ,  $\text{Cl}_2$ ,  $\text{Br}_1\text{Cl}_2$ ,  $\text{Br}_2\text{Cl}_2$ ,  $\text{Cl}_3$ ,  $\text{Br}_1\text{Cl}_3$ ,  $\text{Br}_2\text{Cl}_3$ , and  $\text{Br}_3\text{Cl}_3$  compounds. Enter this data into Table 1 next to the appropriate formula in the column labeled relative intensities. You may use a graphing calculator, or the shorthand procedure,<sup>4</sup> to generate the coefficients. The 9:15:7:1 cluster for  $\text{Br}_1\text{Cl}_2$  is already entered in Table 1.

**Problem 2:** Enter L:R in the next column for each cluster in Table 1.

**Problem 3:** Complete Table 1 by entering the data indicated in the remaining columns. **Answers to Problems 1-3:** The gray entries in columns 2-7 of Table 1.<sup>5</sup>

**Table 1. Data for ideal  $\text{Br}_m\text{Cl}_n$  compounds**

Formula	Relative Intensities	L:R	$n$	$m$	$m + n$	$M$
$\text{Br}_1$	1:1	1:1	0	1	1	2
$\text{Br}_2$	1:2:1	1:1	0	2	2	3
$\text{Br}_3$	1:3:3:1	1:1	0	3	3	4
$\text{Cl}_1$	3:1	3:1	1	0	1	2
$\text{Br}_1\text{Cl}_1$	3:4:1	3:1	1	1	2	3
$\text{Br}_2\text{Cl}_1$	3:7:5:1	3:1	1	2	3	4
$\text{Cl}_2$	9:6:1	9:1	2	0	2	3
$\text{Br}_1\text{Cl}_2$	9:15:7:1	9:1	2	1	3	4
$\text{Br}_2\text{Cl}_2$	9:24:22:8:1	9:1	2	2	4	5
$\text{Cl}_3$	27:27:9:1	27:1	3	0	3	4
$\text{Br}_1\text{Cl}_3$	27:54:36:10:1	27:1	3	1	4	5
$\text{Br}_2\text{Cl}_3$	27:81:90:46:11:1	27:1	3	2	5	6

**Problem 4:** Find which of the three variables,  $n$ ,  $m$ , or  $M$ , causes the ratio L:R to change. **Answer:**  $n$ .

**Problem 5:** Place the symbol (i.e.,  $n$ ,  $m$  or  $M$ ) for the variable you found in Problem 4 in the box just above L:R in Table 2. Then enter the appropriate values for this variable from Table 1 into the appropriate columns of Table 2.

**Answer:** The gray entries in columns 1-5 of Table 2.

**Table 2. The correlation of L:R with a variable**

$n$	0	1	2	3	4	5	$n$
L:R	1:1	3:1	9:1	27:1	81:1	243:1	$3^n$

**Problem 6:** The objective is to find how the variable you entered across the top of Table 2 varies with the ratio L:R. Because R is a constant 1 for all ideal clusters, the ratio L:R = L:1 = L. Determine how the variable is mathematically related to L and place your result in the last column of Table 2. **Answer:**  $3^n:1 = \text{L:R}$ , which simplifies to  $3^n = \text{L}$  when  $R = 1$ . This generalized result is the last entry in Table 2.

**Problem 7:** Extrapolate the pattern established by the first four sets of numerical entries in Table 2 to find L:R for the next two values of the variable and add this data to the remaining two columns in Table 2. **Answer:** 81:1 for  $n = 4$ , and 243:1 for  $n = 5$ . These results are entered into columns 6-7 of Table 2.

**Problem 8:** Write a short statement that explains how L varies with the variable you found. **Answer:** The intensity of the leftmost cluster peak increases by a factor of three with the addition of each chlorine atom.

**Problem 9:** The solutions to Problems 6 and 8, respectively, give a chlorine rule in symbols and words. Use your empirically derived rule to determine the number of Cl atoms in a  $\text{Br}_m\text{Cl}_n$  compound for which the cluster is 81:189:162:66:13:1. **Answer:**  $3^n = 81$ ,  $n = 4$ .

**Problem 10:** Derive an equation from the data in Table 1 that shows  $m$  as a function of  $M$  and  $n$ . **Answer:**  $M = m + n + 1$ ;  $m = M - 1 - n$  or  $m = M - (n + 1)$ .

**Problem 11:** Determine the number of Br atoms in the compound of Problem 9. **Answer:** The cluster contains 6 peaks, or  $M = 6$  and  $m = 6 - 5 = 1$ . The compound contains four chlorine atoms plus one bromine atom; it is a  $\text{Br}_1\text{Cl}_4$  compound.

**Problem 12:** Find  $n$  and  $m$  for the  $\text{Br}_m\text{Cl}_n$  compound that produces the cluster and tabulated relative abundances shown in Figure 2.

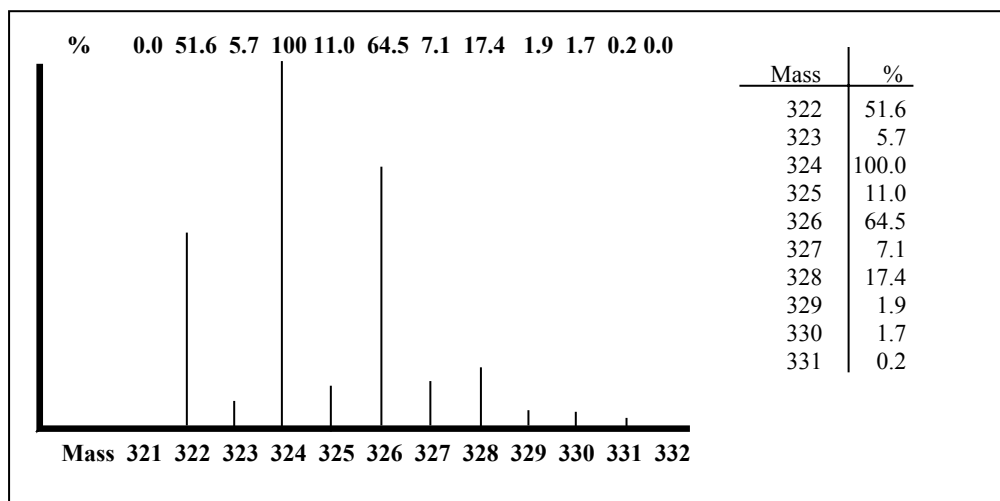


Figure 2. Isotope pattern and table of relative abundances<sup>2</sup> for an unknown  $\text{Br}_m\text{Cl}_n$  compound.

**Answer:**  $L:R = 51.6/1.7 = 30 \approx 27$  or  $n = 3$ ,  $m = 1$ . The mathematical solution gives  $3^n = 30$  or  $n = 3.1$ , and  $n$  must be a whole number. Alternatively, 30 is much closer to 27 than it is to 81, so  $n = 3$ . The value of  $m$  is found by subtracting  $n + 1$  or 4 from 5, the number of peaks  $M$  in the cluster, to give 1. It is a  $\text{Br}_1\text{Cl}_4$  compound.

**Problem 13:** The unknown in problem 12 is a  $\text{C}_{10}$  saturated, acyclic compound that contains only chlorine, bromine, carbon and hydrogen. Use the mass of 322 for L and determine the molecular formula of the unknown from your values of  $n$  and  $m$ . Enter the formula into Yan's isotope calculator found on the Internet at:

<http://www.geocities.com/junhuayan/pattern.htm>. When the data generated by the computer matches the data in Figure 2, your formula is correct and you have completed the exercise. **Answer:**  $\text{C}_{10}\text{H}_{18}\text{Br}_1\text{Cl}_3$ .

### Analysis

Twenty-two of 23 students who participated in phase one, the guided-inquiry exercise, were able to formulate the chlorine rule and find the correct values for  $n$  and  $m$  for the cluster 81:187:162:66:13:1. Handout 1 was modified after its first use (e.g., the cluster pattern 9:15:7:1 was placed in Table 1 to show students exactly what

was being asked). Problem 12 was also added to introduce students to the evaluation of a cluster as it appears in a mass spectrum and to introduce them to an isotope pattern calculator. In phase one of the study, students learn what the chlorine rule is. In the second phase, they learn how to apply it to actual spectra of real compounds.

In phase two, students were given Handout 2 entitled, “Application of the Chlorine Rule.” This handout includes three spectra for students to analyze at home. Answers<sup>5</sup> are provided herein but were given to students only after they had completed the assignment.

### **Application of the Chlorine Rule (Handout 2)—Phase 2**

Several steps are required to successfully analyze real  $\text{Br}_m\text{Cl}_n$  molecular-ion clusters. They include: locating the cluster and determining its nature (i.e., whether it is a symmetrical or asymmetrical cluster and whether it is normal or abnormal in appearance), assessing the cluster by normalizing it to find L:R, determining values for  $n$  and  $m$ , and validating the final answer. With practice, you will instinctively know what to do. Until then, the following procedure provides a step-by-step guide to help you get started.

#### **1. Identify the cluster**

##### **A. Location of the cluster in the mass spectrum**

Because the cluster represents molecular ions, the cluster will normally be the rightmost group of peaks in the spectrum. If a prior fragmentation has occurred and the apparent cluster in the spectrum does not represent molecular ions, you will be given the true value of  $M$  and you must account for the intervening masses between the apparent cluster and the true  $M$ .

##### **B. Nature of the cluster**

A normal cluster contains  $m + n + 1$  molecular ions two mass units (i.e., amu or daltons) apart. The cluster begins with the lowest-mass molecular ion  $M$  and includes ions of masses  $M + 2$ ,  $M + 4$ , etc., until the  $m + n + 1$  requirement is met. In general, a cluster that begins on the peak of an even mass ion includes all visible even numbered molecular-ion peaks. Clusters may be characterized as symmetrical or asymmetrical. Ideal compounds that contain bromine as the only  $A + 2$  element generate perfectly symmetrical clusters, and the clusters of the corresponding real compounds are so near symmetrical that they can easily be distinguished from the clusters of chlorine containing compounds, which are always asymmetrical. The symmetry of  $\text{Br}_m$  clusters arises from the symmetry inherent in the near 1:1 ratio of bromine isotopes. The asymmetry of  $\text{Br}_m\text{Cl}_n$  clusters arises from the 3:1 ratio of chlorine isotopes. Figure 1 shows the expected clusters for  $\text{Br}_1$  to  $\text{Br}_6$  compounds.

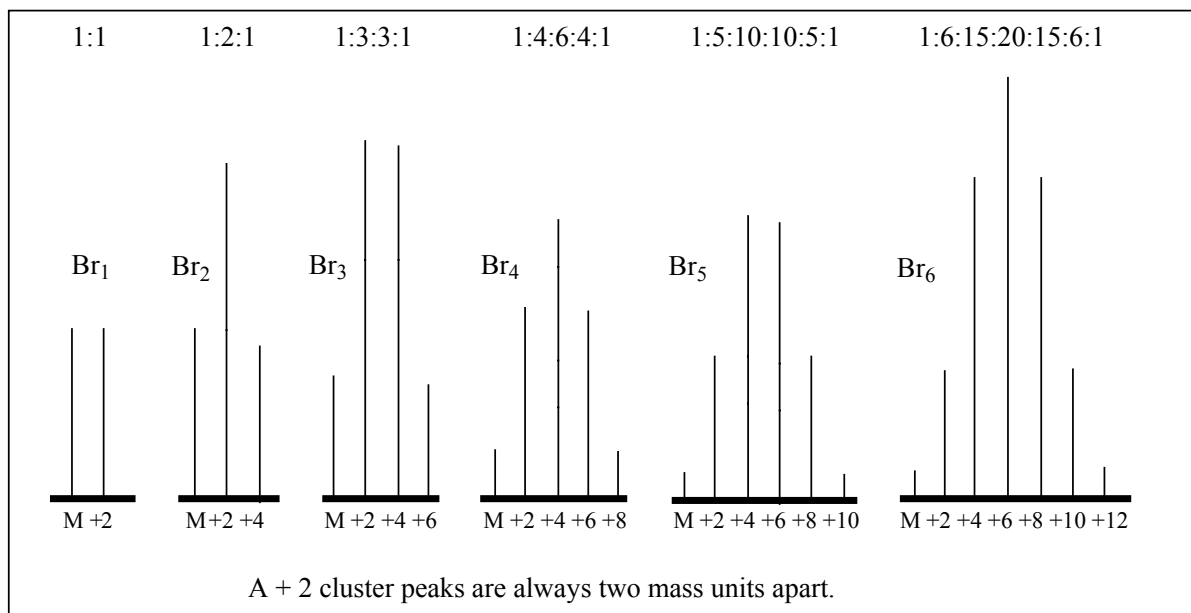


Figure 1. Clusters of peaks from ions containing bromine as the only A + 2 element.

For these clusters,  $m = M - 1$ , or the number of bromine atoms  $m$  is always one less than the number of peaks  $M$  in symmetrical clusters, providing all cluster peaks are visible. Note the shape and the repeating nature of the bromine clusters. Starting with  $\text{Br}_1$ , compounds with an odd  $m$  subscript (i.e.,  $\text{Br}_1$ ,  $\text{Br}_3$  and  $\text{Br}_5$ ) produce clusters that contain two central peaks (twin towers) of near equal intensity. Whereas, compounds with an even  $m$  subscript (i.e.,  $\text{Br}_2$ ,  $\text{Br}_4$  and  $\text{Br}_6$ ) produce clusters that contain a single peak of strong intensity (spire) that lies in the center of the symmetrical cluster. Real bromine clusters are not perfectly symmetrical but are easily recognizable as bromine only clusters by their near symmetry. Note also that the second term in the isotope pattern equals  $m$  for that pattern. For example, for  $m = 5$ , the second peak in the cluster should be five times as intense as the first and last peaks. This relationship can be used to validate an analysis, as will be seen below.

The appearances of the three kinds of chlorine clusters that are most often encountered are shown in Figure 2. The cluster peaks in each case are shown in black; other peaks that share the molecular-ion region of the spectrum but are not A + 2 cluster peaks are shown in gray.

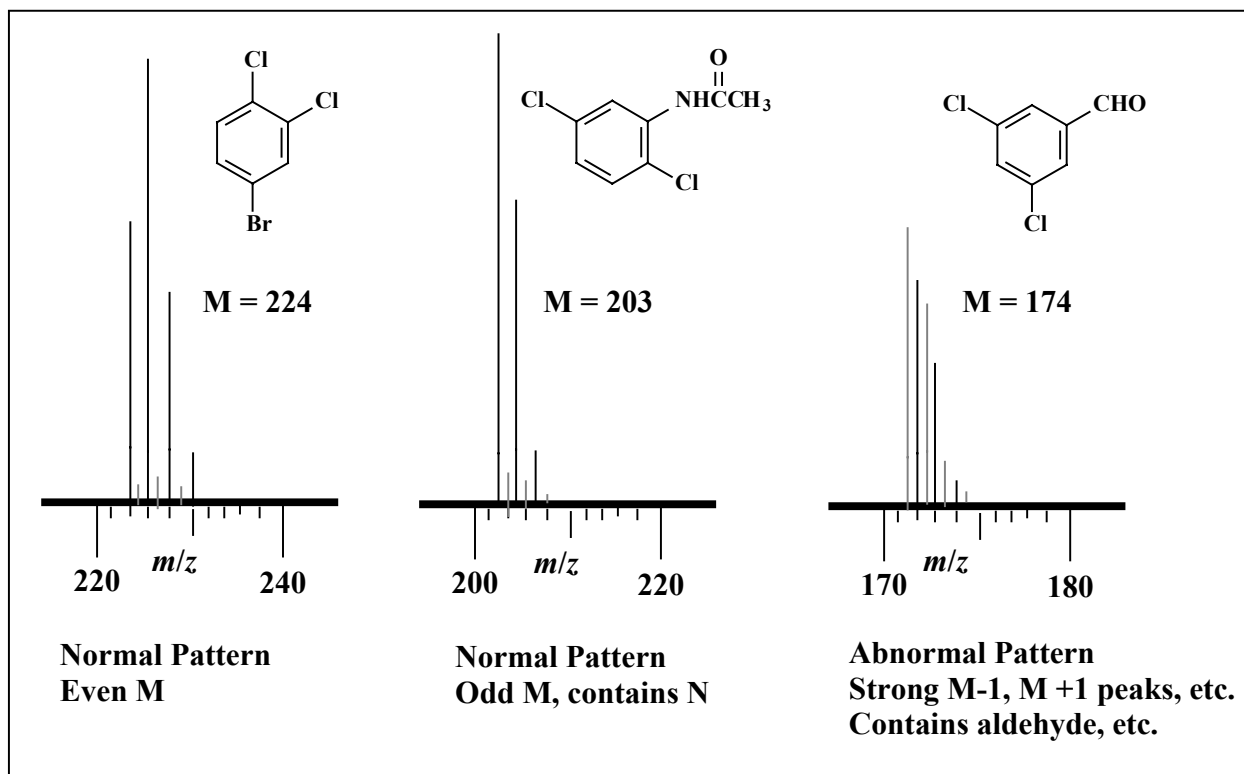


Figure 2. Three typical isotope patterns of chlorine containing compounds.

Because  $M$  for compounds that do not contain nitrogen is an even number, all peaks in a normal cluster such as the left cluster in Figure 2, will be due to even-mass molecular ions. The cluster will stand out, because the intensities of the cluster peaks are generally much more intense than those of adjacent peaks due to odd-numbered masses, and cluster peaks are two mass units apart. The exception is the cluster peak of the highest-mass ion, which is critical to the analysis. It is sometimes very small, and care must be taken to measure it as accurately as possible. Special techniques may be required to ensure you have the correct cluster.

When one nitrogen atom is present in the sample, as shown in the center cluster of Figure 2, the cluster will appear normal. However, every peak in the cluster appears at an odd  $m/z$  value, and the intervening peaks appear at even  $m/z$  values. As Figure 2 shows, the chlorine rule and nitrogen rule are independent; both may be applied independently to the same cluster. The odd value of  $M = 203$  signals the presence of an odd number of nitrogen atoms. Our compounds will never contain more than one nitrogen atom.

When the unknown is an aldehyde, a strong  $M - 1$  peak is probably visible in the mass spectrum due to the fragment ion produced by the loss of the aldehydic hydrogen atom. The third cluster in Figure 2 is that of an aldehyde. Other organic families such as alcohols and toluene derivatives might also fragment by loss of a hydrogen

atom to produce an  $M - 1$  peak. The apparent cluster will start at an odd  $M - 1$  mass and consist of a series of peaks one mass unit apart. The real molecular-ion cluster starts at  $M$  and excludes the peaks that are characteristic of aldehydes, etc., even though they are normally very intense peaks. As a general rule, identify  $M$  and consider every  $M + 2$ ,  $M + 4$ ,  $M + 6$ , etc., peak to be part of the cluster.

## 2. Assess the Cluster

### A. Locate L and R

After the cluster is identified, only two peaks in the cluster are important for finding the number of chlorine atoms; they are the leftmost peak L and the rightmost peak R in the cluster.

### B. Normalize the Cluster

Determine the peak heights of L and R (e.g., in millimeters; the more precisely, the better) and divide the height of L by the height of R. The dimensionless quotient is the normalized intensity of L or  $I_M$ . This is the key step, because the stoichiometry is most evident in a normalized cluster.

### C. Find $n$

The practical limit to the number of chlorine atoms in our samples is four. When a sample compound contains four chlorine atoms in its formula, the value of  $L/R$  ( $I_M$ ) will be near that of the ideal value 81. The compound contains  $3^n = 81$  or 4 chlorine atoms. Likewise, when the value of  $L/R$  ( $I_M$ ) is near 1, 3, 9, or 27, the corresponding value of  $n$  is 0, 1, 2, or 3. If you find  $L/R$  to be near 22 or 66, your compound probably contains sulfur.<sup>6</sup> If you find a value for  $L/R$  not to be within the ranges 1-2, 3-4, 9-12, 27-34, or 81-100, then you should be sure you are using a cluster peak (i.e., one that is a multiple of 2 daltons more than  $M$ ). If your first R was at an even multiple of 2 higher than  $M$  but gave an abnormal  $I_M$ , then try the peak at  $m/z$  two daltons less than your first trial R.<sup>7</sup>

### D. Find $m$

The number of peaks in a cluster is equal to  $m + n + 1$ . After  $n$  is found,  $m$  is determined by difference. Count the number of peaks in the cluster (e.g., the black peaks in Figure 1). Subtract  $n + 1$  from the number of peaks to find  $m$ .

## 3. Special techniques

### A. No molecular-ion cluster

Sometimes a true value of  $M$  and hence the cluster is not visible in a mass spectrum, because the molecular ions fragment before  $M$  is detected. In these cases, try to determine values of  $n$  and  $m$  from non-molecular-ion clusters, which represent partial structures of the unknown sample. This kind of fragmentation is known to occur in alkyl halides (3). This limits the number of polyhalide derivatives of long-chain alkanes that are available for analysis, and none are in this study. The positive side of the limitation is that the appearance of a molecular-ion cluster is a good indicator of an aryl halide. When a spectrum lacks a molecular-ion cluster, it is sometimes possible to determine  $m$  and  $n$  by inference.

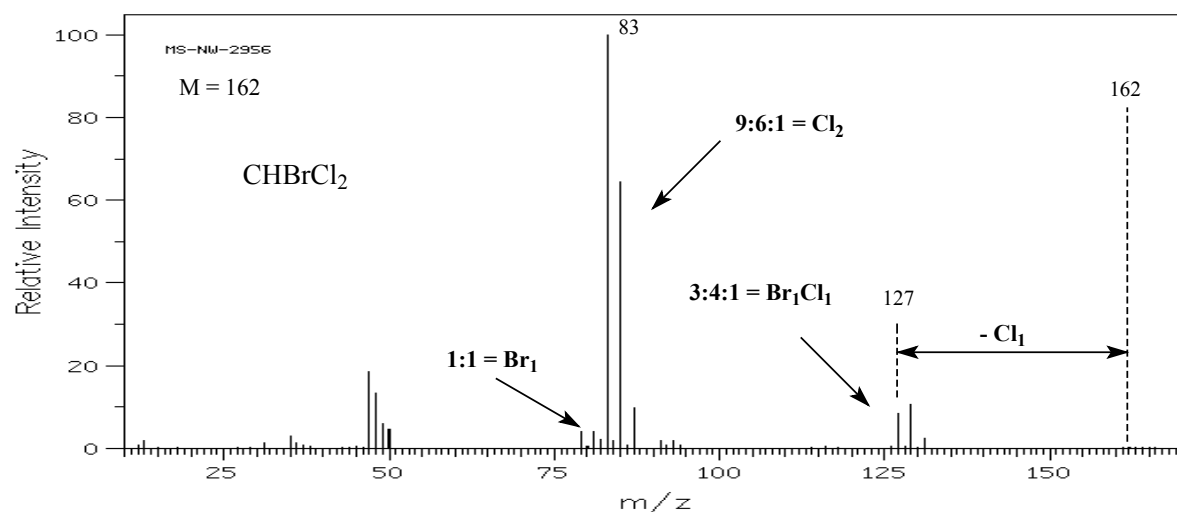


Figure 3. The mass spectrum<sup>8</sup> of bromodichloromethane reprinted from reference 4.

Figure 3 shows the mass spectrum of bromodichloromethane (4), which lacks the molecular-ion cluster predicted by the isotope calculator (See Figure 1, Handout 1). In these problems, when a true  $M$  is not apparent, its  $m/z$  value will be provided in the upper left corner of the spectrum.<sup>9</sup> In this case,  $M = 162$ . This mass provides a basis for analyzing other peaks in the spectrum by the procedure outlined above. An analysis of the 3:4:1 cluster, starting at  $m/z$  127, and the 9:6:1 cluster, starting at  $m/z$  83, shows them to represent  $\text{Br}_1\text{Cl}_1$  and  $\text{Cl}_2$ , respectively. Thus, as a minimum, the compound contains  $\text{Br}_1\text{Cl}_2$ . When the mass of one chlorine atom is subtracted from  $M$ , the result is  $162 - 35 = 127$ , indicating that  $M$  contains one bromine and two chlorine atoms. A doublet of peaks at  $m/z$  79 and 81 attributable to bromine is also present in the spectrum. Note: Intensity data for fragment ions is not always reliable. Two or more distinctly different ions may contribute to the intensity of a peak because they have identical masses.

## B. Ultra-tiny peaks

The value of  $I_M$  for an ideal  $\text{Cl}_4$  compound is 81; for a real  $\text{Cl}_4$  compound, the value is even higher (e.g.,  $\sim 100$ ). Thus, four chlorine atoms define the practical limit for this kind of analysis. Figure 4 shows the mass spectrum of the real  $\text{Cl}_4$  compound 1,2,3,4-tetrachloro-5-nitrobenzene.

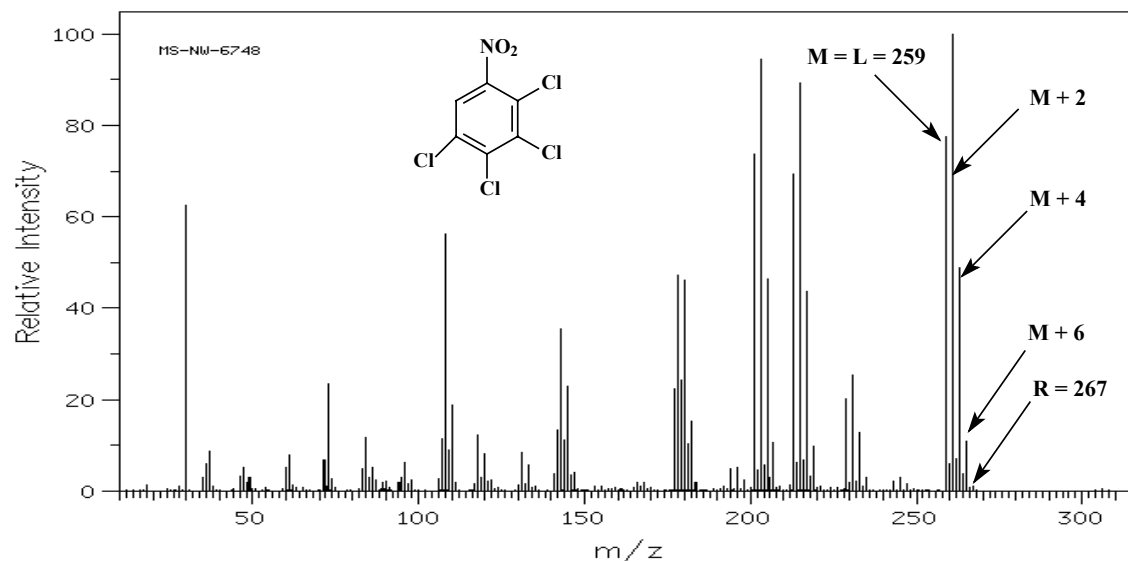


Figure 4. The mass spectrum<sup>8</sup> of 1,2,3,4-tetrachloro-5-nitrobenzene reprinted from reference 4.

Does the cluster that starts at  $m/z$  259 contain four or five peaks? It's asymmetrical, so it contains chlorine. It's clear that the left peak L is at  $m/z$  259, but is the right peak R at  $m/z$  265 or 267? An ultra-tiny peak (i.e., less than 1%) is at  $m/z$  267. The 267 peak is slightly more intense than the 266 peak; this is a clue that this ultra-tiny peak belongs to the cluster. One way to decide whether the cluster ends at  $m/z$  265 or 267 is to find  $m$  and  $n$  for a four-peak and for a five-peak cluster. The peak heights of the peaks at  $m/z$  259, 265 and 267 are measured. The height of the peak at  $m/z$  259 is  $h_{259} = 75$  mm. Likewise,  $h_{265} = 10.5$  mm and  $h_{267} = 1$  mm. Then,  $I_{259}/I_{265} = 75 \text{ mm}/10.5 \text{ mm} = 7.1$  and  $I_{259}/I_{267} = 75$ . The nearest model-allowed values for these ratios are 9 and 81, respectively. These ratios give  $\text{Br}_1\text{Cl}_2$  for the four-peak cluster and  $\text{Cl}_4$  for the five-peak cluster. To decide between the two possible formulas, the binomial pair for each is expanded by the shorthand method, so the ratios of the first two peaks in the ideal clusters may be compared to the first two molecular-ion peaks in the spectrum. For  $\text{Br}_1\text{Cl}_2$ , the binomial pair is  $(1:1)(3:1)^2 = 9:15:7:1$ . For  $\text{Cl}_4$ , the binomial pair is  $(3:1)^4 = 81:108:54:12:1$ . Only the first two peaks will be compared. For  $\text{Br}_1\text{Cl}_2$ , the second peak is  $15/9 = 1.7$  times more intense than the first. For  $\text{Cl}_2$ , this ratio is  $108/81 = 1.3$ . The corresponding ratio from the spectrum is  $97/75 = 1.3$ . Thus, this analysis shows the spectrum to represent a  $\text{Cl}_4$  and not a  $\text{Br}_1\text{Cl}_2$  compound; it is a five-peak spectrum. The actual compound is 1,2,3,4-tetrachloro-5-nitrobenzene; the

value of L:R from the corresponding relative abundance data<sup>2</sup> is  $L:R = 77.8/0.9 = 80$ . Verification is recommended anytime an ultra-tiny peak is encountered.

#### 4. Verification

##### A. Chlorine compounds

Once you determine values for  $m$  and  $n$ , you may solve the binomial pair for  $(1:1)^m(3:1)^n$  and compare the resulting cluster with the cluster in the spectrum. A comparison of the first two peaks, as in the previous example, is often sufficient. The entire cluster may be compared if necessary.

##### B. Bromine compounds

The Pascal-triangle nature of the bromine-only clusters is such that the height of the second peak is always  $m$  times higher than the first and last for ideal cluster peaks. Therefore, the height of the second peak divided by the height of the first for real bromine-only compounds gives an approximate value of  $m$  directly from the spectrum. The spectrum in Figure 5 below represents hexabromobenzene. The seven-peak cluster is not confused with a five-peak cluster, because the second peak is 6 times the first; whereas, the third is only about 2.5 times the second. This latter value cannot satisfy five peaks. Thus, the cluster contains seven peaks, which represent a  $\text{Br}_6$  compound.

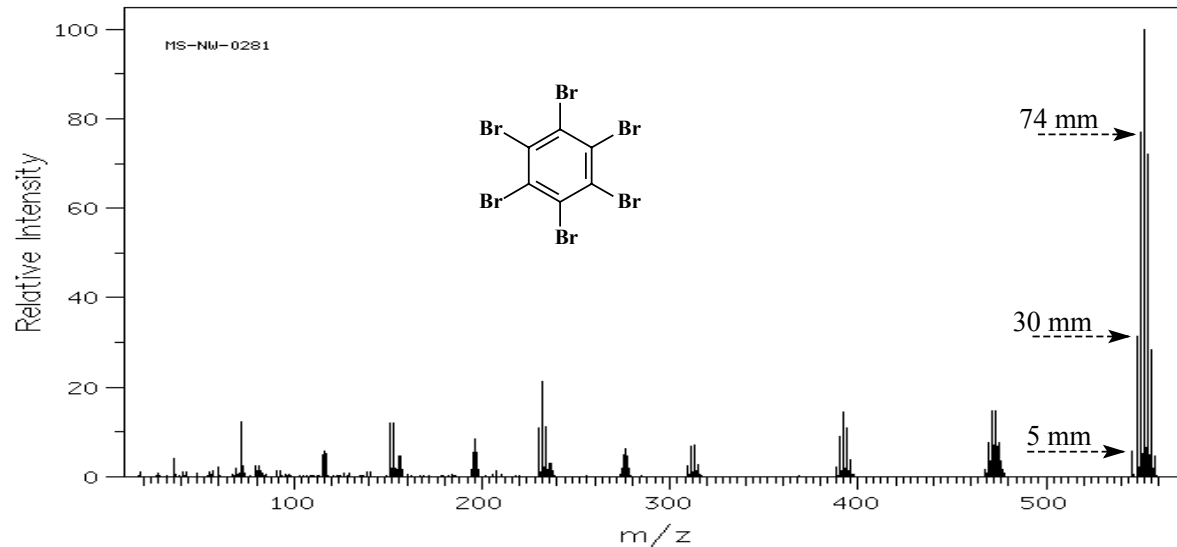


Figure 5. The mass spectrum<sup>8</sup> of hexabromobenzene reprinted from reference 4.

**Problems 1-3:** Apply the methodology to the mass spectra in Figures 6-8. Find values for  $n$  and  $m$  for the unknown compounds 1-3. Additionally, complete as much of each structure as possible from the mass spectrum. Determine whether or not the formula contains one N atom<sup>10</sup> and whether or not the compound contains a structural feature such as CHO (aldehyde), OH (alcohol), or toluene derivative that gives a strong  $M - 1$  peak.

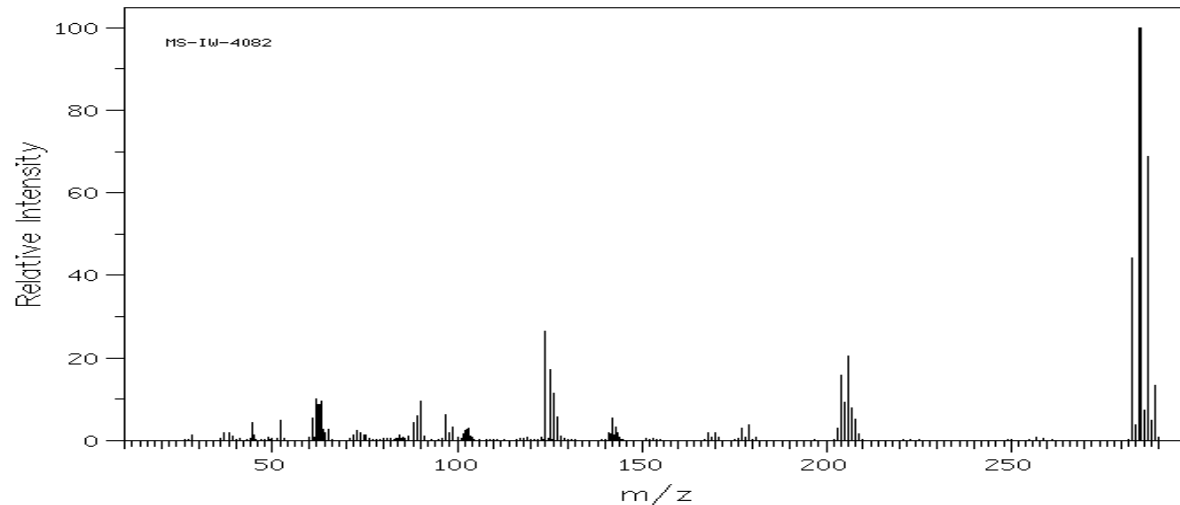


Figure 6. The mass spectrum<sup>8</sup> of Unknown 1, a  $\text{Br}_m\text{Cl}_n$  compound reprinted from reference 4.

**Solution 1:** The asymmetric four-peak cluster pattern is normal and begins with M at  $m/z = 283$  (odd). The asymmetric cluster indicates chlorine, and the sample contains an odd number of nitrogen atoms because M is an odd number.  $L_{283} = 38$  mm and  $R_{289} = 11.5$  mm;  $I_M = L:R = 38/11.5 = 3.3$ . Therefore,  $n = 1$ .  $M = 4$ ;  $m = 4 - 2 = 2$ . The unknown contains  $\text{Br}_2\text{Cl}_1\text{N}_1$ . Validation:  $(1:1)^2(3:1) = 3:7:5:1$ , which matches the cluster.

**Additional analysis:** The mass of  $\text{Br}_2\text{Cl}_1\text{N}_1$  is 207.  $M - 207 = 283 - 207 = 76$ . The likely residue of mass 76 is  $\text{C}_6\text{H}_4$ , indicating a benzene derivative. The compound is probably a constitutional isomer of dibromochloroaniline. The actual structure is 2,6-dibromo-4-chloroaniline; it is the structure on the left in Figure 9 below.

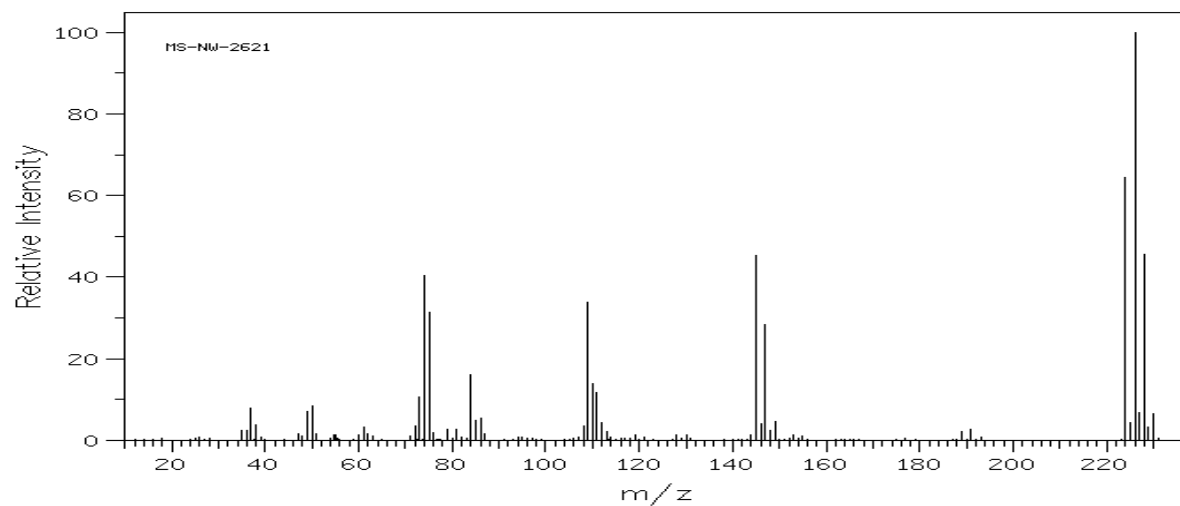


Figure 7. The mass spectrum<sup>8</sup> of Unknown 2, a  $\text{Br}_m\text{Cl}_n$  compound reprinted from reference 4.

**Solution 2:** The asymmetric four-peak cluster is normal and begins at  $m/z$  224. Chlorine is present, and nitrogen is not apparent.  $L = 55$  mm and  $R = 5$  mm.  $I_M = L/R = I_{224}/I_{230} = 34.5/3.5 = 9.9$ ,  $n = 2$ .  $M = 4$ ;  $m = 4 - 3 = 1$ . The unknown contains  $\text{Br}_1\text{Cl}_2$ . Validation:  $(1:1)(3:1)^2 = 9:15:7:1$ , which is observed in the spectrum.

**Additional analysis:** The mass of  $\text{Br}_1\text{Cl}_2$  is 149.  $M - 149 = 224 - 149 = 75$ . The likely residue of mass 75 is  $\text{C}_6\text{H}_3$ , indicating a benzene derivative. The compound is probably a constitutional isomer of bromodichlorobenzene. The actual structure is 1-bromo-2,3-dichlorobenzene; it is the center structure in Figure 9.

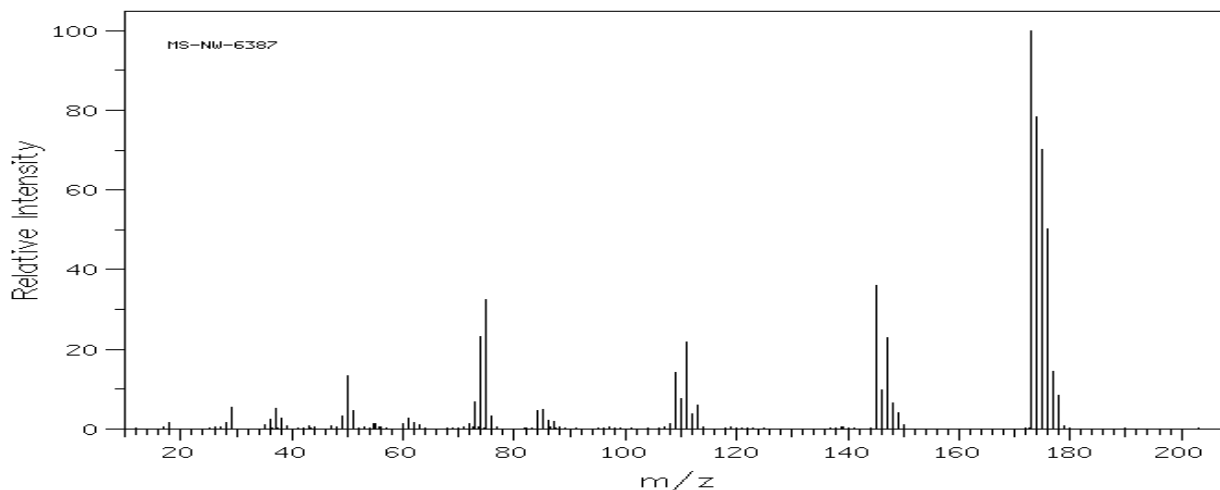


Figure 8. The mass spectrum<sup>8</sup> of Unknown 3, a  $\text{Br}_m\text{Cl}_n$  compound reprinted from reference 4.

**Solution 3:** The appearance of the cluster is abnormal (i.e., major peaks are separated by 1 amu), indicating the presence of a group that produces a strong  $M - 1$  peak. Thus, the peak at  $m/z = 173$  is due to  $M - 1$ , and the three-peak cluster begins at  $m/z$  174. Nitrogen is probably not present (if N were present, M would start on an odd  $m/z$  and the  $M - 1$  peak would represent an even mass).  $L_{174} = 67.5$  mm and  $R_{178} = 7.0$  mm;  $I_M = L/R = 67.5/7.0 = 9.6$ ,  $n = 2$ .  $M = 3$ ;  $m = 3 - 3 = 0$ . The unknown contains  $\text{Cl}_2$  and a group that gives a strong  $M - 1$  peak. Validation:  $(3:1)^2 = 9:6:1$ , which is the characteristic  $\text{Cl}_2$  cluster.

**Additional analysis:** The strong peak at  $m/z$  145 is probably due to the loss of 29 ( $\text{CHO} = -\text{H}$  and  $-\text{CO}$ ) from  $M = 174$ . The mass of  $\text{Cl}_2 + \text{CHO}$  is 99.  $M - 99 = 174 - 99 = 75$ , indicating a benzene derivative. The compound is probably a constitutional isomer of dichlorobenzaldehyde.<sup>11</sup> The actual structure is 3,5-dichlorobenzaldehyde; it is the structure on the right side of Figure 9.

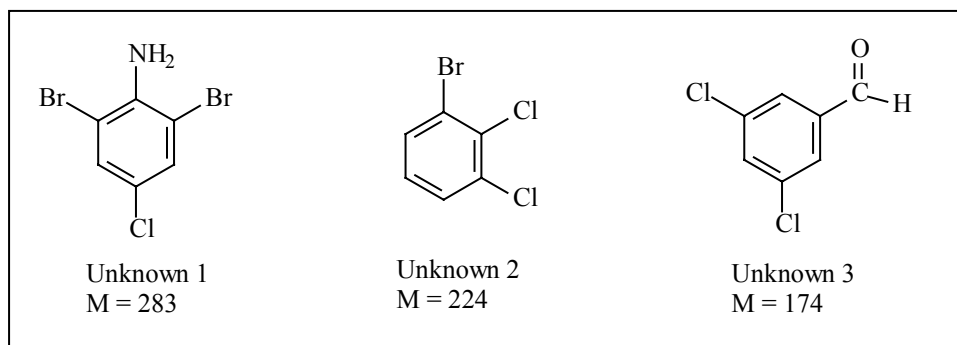


Figure 9. Structures of 2,6-dibromo-4-chloroaniline, 1-bromo-2,3-dichlorobenzene and 3,5-dichlorobenzaldehyde, unknowns 1-3, respectively.

### Phase 3

After completion of their homework assignment, students were given solutions to the three problems above, and phase two of the study was complete. In phase three, students were given six mass spectra for analysis during a laboratory period. All formulas analyzed contained at least two halogen atoms. The student-analyzed compounds are shown in Tables 1-3. Table 1 contains the names of compounds that contain only C, H, Br and Cl in the formulas. Table 2 includes compounds that contain oxygen but no nitrogen, and Table 3 contains the names of any compounds that contain nitrogen. The numbers in the column headed T indicate the total number of times a given spectrum was analyzed by students who were enrolled in an organic chemistry II laboratory.

The student group that comprised phases two and three of the study differed slightly from the group that participated in phase one. Two students who were not enrolled in the laboratory section did not participate in phases three and four. Four new students were allowed to join the study. Thus, twenty-five students participated in phases two and three of the study. The newcomers were given the two handouts for home study, and then they analyzed six spectra along with the other 21 students during a laboratory period. The 25 students required 150 spectra in order for each spectrum to be analyzed a minimum of two times each.

**Table 1. Hydrocarbon derivatives<sup>12</sup> analyzed by the chlorine rule**

Br <sub>m</sub> Cl <sub>n</sub>	Name	T	A	B	CAS Registry Number	SDBS No.	Spec. No.
Cl <sub>4</sub>	1,2,3,4-tetrachlorobenzene	5		2	634-66-2	1546	1884
Cl <sub>3</sub>	1,2,3-trichlorobenzene	2	2		87-61-6	546	1873
BrCl <sub>2</sub>	1-bromo-2,3-dichlorobenzene	2	2		56961-77-4	5446	2621
BrCl <sub>2</sub>	1-bromo-2,4-dichlorobenzene	3	2		1193-72-2	15809	7683
BrCl <sub>2</sub>	2-bromo-1,3-dichlorobenzene	2	2		19393-92-1	5448	2798
BrCl <sub>2</sub>	2-bromo-1,4-dichlorobenzene	2	2		1435-50-3	5447	6106

Br <sub>3</sub>	tribromomethane (bromoform)	5	2	2	75-25-2	1307	3681
Br <sub>2</sub> Cl	1,2-dibromo-3-chloropropane*	2	1		96-12-8	2013	9152
BrCl	<i>o</i> -bromochlorobenzene	2	2		694-80-4	2011	0837
BrCl	<i>p</i> -bromochlorobenzene	3	2		106-39-8	1494	2079
Br <sub>4</sub>	1,1,2,2-tetrabromoethane	4	1	2	79-27-6	3412	4430
BrCl <sub>2</sub>	4-bromo-1,2-dichlorobenzene	2	2		18282-59-2	5449	3241
Cl <sub>3</sub>	1,3,5-trichlorobenzene	4	1	2	108-70-3	73	1393
Cl <sub>3</sub>	1,2,4-trichlorobenzene	2	2		120-82-1	2866	0787
BrCl	<i>m</i> -bromochlorobenzene	2	2		108-37-2	3012	0872
Cl <sub>4</sub>	1,2,3,5-tetrachlorobenzene	2	1		634-90-2	1521	8753
Cl <sub>4</sub>	1,2,4,5-tetrachlorobenzene	2	1		95-94-3	1114	1386
Br <sub>4</sub>	1,2,4,5-tetrabromobenzene	4	1	2	636-28-2	1113	0267
Br <sub>6</sub>	hexabromobenzene	2	2		87-82-1	1449	0281
Cl <sub>2</sub>	dichloromethane	2	2		75-09-2	891	5526
Br <sub>2</sub>	dibromomethane	3	2		74-95-3	2171	4074
BrCl <sub>3</sub>	1-bromo-2,3,5-trichlorobenzene	4		1	81067-38-1	16819	0278
BrCl <sub>2</sub>	bromodichloromethane*	6		2	75-27-4	5235	2956

**Table 2. Oxygenated compounds<sup>12</sup> analyzed by the chlorine rule**

Br <sub>m</sub> Cl <sub>n</sub>	Name	T	A	B	CAS Registry Number	SDBS No.	Spec. No.
Br <sub>2</sub> O	2,4-dibromophenol	3	1		615-58-7	10732	1651
Br <sub>2</sub> O	2,6-dibromophenol	3		1	608-33-3	21778	7581
Br <sub>3</sub> O	2,4,6-tribromophenol	5		3	118-79-6	1507	0292
Br <sub>3</sub> O	2,3,5-tribromophenol	5		2	57383-81-0	33867	2491
Cl <sub>3</sub> O	2,4,6-trichlorophenol	2	2		88-06-2	1446	0282
Cl <sub>3</sub> O	3,4,5-trichlorophenol	2	2		609-19-8	13766	6716
BrClO	2-bromo-4-chlorophenol	2	2		695-96-5	15131	7114
BrClO	4-bromo-2-chlorophenol	3	2		3964-56-5	15132	9719
Cl <sub>3</sub> O <sub>2</sub>	trichloroacetic acid*	4			76-03-9	3138	1364
Cl <sub>2</sub> O <sub>2</sub>	2,4-dichlorobenzoic acid	2	2		50-84-0	2084	1858
Cl <sub>2</sub> O <sub>2</sub>	3,4-dichlorobenzoic acid	3	3		51-44-5	3420	4797
Cl <sub>2</sub> O <sub>2</sub>	3,5-dichlorosalicylaldehyde	3	3		90-60-8	3442	4800
Cl <sub>2</sub> O <sub>2</sub>	3,5-dichlorobenzoic acid	2	2		51-36-5	3445	4802
Cl <sub>2</sub> O <sub>2</sub>	2,5-dichlorobenzoic acid	2	2		50-79-3	5591	3242
Cl <sub>2</sub> O <sub>2</sub>	2,6-dichlorobenzoic acid	4	1	2	50-30-6	10744	1654
Cl <sub>2</sub> O <sub>2</sub>	ethyl 2,5-dichlorobenzoate	2	2		35112-27-7	16767	0166
BrClO	<i>m</i> -bromobenzoyl chloride	2	1		1711-09-7	5579	5368
Cl <sub>2</sub> O	2,6-dichlorobenzaldehyde	2	1		83-38-5	667	4768
Cl <sub>2</sub> O	<i>o</i> -chlorobenzoyl chloride*	2	1		609-65-4	1952	0866
Cl <sub>2</sub> O	3,5-dichlorobenzaldehyde	4		2	10203-08-4	2846	6387
BrClO	2-bromo-4'-chloroacetophenone	2	2		536-38-9	6084	3526
Cl <sub>2</sub> O	2',5'-dichloroacetophenone	2	2		2476-37-1	16666	9449
Cl <sub>2</sub> O	2',4'-dichloroacetophenone	2	2		2234-16-4	3065	2852
Cl <sub>3</sub> O	2,2',4'-trichloroacetophenone*	5		2	4252-78-2	13760	8929
Cl <sub>3</sub> O	2',3',4'-trichloroacetophenone	5		1	13608-87-2	13761	6755
Cl <sub>2</sub> O	4,4'-dichlorobenzophenone	2	2		90-98-2	12986	6485
Br <sub>2</sub> O <sub>2</sub>	methyl 3,5-dibromobenzoate	5	1	1	51329-15-8	16194	8142
Br <sub>2</sub> O <sub>2</sub>	3,7-dibromo-2-methoxy-2,4,6-cycloheptatrien-1-one	4		2	33695-99-7	33031	5939
Br <sub>5</sub> O	pentabromophenol	4	-	1	608-71-9	10210	1630

**Table 3. Nitrogen containing compounds analyzed by the chlorine rule**

Br <sub>m</sub> Cl <sub>n</sub>	Name	T	A	B	CAS Registry Number	SDBS No.	Spec. No.
	Nitrogen						
Cl <sub>2</sub> N	2,6-dichloroaniline	2	2		608-31-1	1541	1866
Cl <sub>2</sub> N	2,4-dichloroaniline	2	2		554-00-7	2091	1854
Cl <sub>2</sub> N	2,5-dichloroaniline	4	1	2	95-82-9	2092	1859
Cl <sub>3</sub> N	2,4,6-trichloroaniline	5	2	2	634-93-5	1500	8752
Cl <sub>3</sub> N	2,3,4-trichloroaniline	2	2		634-67-3	5457	3247
Cl <sub>3</sub> N	3,4,5-trichloroaniline	4	3		634-91-3	23657	0656
Br <sub>2</sub> ClN	2,6-dibromo-4-chloroaniline	3	2		874-17-9	19155	4082
	Nitrogen and oxygen						
Cl <sub>2</sub> NO	2',5'-dichloroacetanilide	2	1		2621-62-7	6103	4992
Cl <sub>2</sub> NO	3',4'-dichloroacetanilide	2	2		2150-93-8	25424	2013
Cl <sub>2</sub> NO	2'4'-dichloroacetanilide	2	2		6975-29-7	34957	4339
Br <sub>2</sub> NO <sub>2</sub>	1,4-dibromo-2-nitrobenzene	2	1		3460-18-2	10298	1241
Br <sub>2</sub> NO <sub>2</sub>	1,2-dibromo-4-nitrobenzene	4		2	5411-50-7	17098	3909
Cl <sub>3</sub> NO <sub>2</sub>	1,3,5-trichloro-2-nitrobenzene	2	2		18708-70-8	10186	1416
Cl <sub>3</sub> NO <sub>2</sub>	1,2,3-trichloro-4-nitrobenzene	2	2		17700-09-3	22811	9646
Cl <sub>4</sub> NO <sub>2</sub>	1,2,3,4-tetrachloro-5-nitrobenzene	3	1		879-39-0	13701	6748
Cl <sub>2</sub> NO <sub>2</sub>	3,5-dichloroanthranilic acid	2	2		5980-23-4	3415	5475
Cl <sub>2</sub> NO <sub>2</sub>	2,6-dichloro-3-nitrotoluene	2	2		29682-46-0	18968	3628

Two copies of the spectra such as those shown in figures 5-8 of the 68 compounds were reproduced, giving 136 spectra for analysis. The remaining 14 spectra were selected and mixed in at random so that each student had 6 spectra to analyze. Spectra that were correctly analyzed for *m* and *n* were recorded under column A of tables 1-3. The students correctly analyzed 56 of the 68 spectra, leaving 12 spectra that were incorrectly analyzed. The misses revealed three major reasons why a student analysis failed. Handout 2 was revised into its current form by the addition of sections 3 and 4.

The topics added to Handout 2 subsequent to phase three include those about bromine-only compounds, fragmentations that leave no real cluster, ultra-tiny R peaks, and the verification procedure. These changes were made pursuant to the notion that students could do better if they knew what to look for in a spectrum. Many of the spectra of the Br<sub>*m*</sub> compounds, which should be among the easiest to analyze, were miss-analyzed in phase three. Some students expected chlorine to be in every compound. A few examples of spectra with no discernible molecular-ion cluster but with daughter clusters that could be analyzed were included in the 68 spectra. No special guidance was given to the students for these spectra before phase three; the only "hint" was the true value of M, which was posted in the upper left corner of the spectrum. Students had to see it (e.g., M = 162) and know what it meant in order to use the value of M to find a latent Br or Cl atom. All but one of these spectra were incorrectly

analyzed because students didn't know how to account for missing masses by analyzing the fragment peaks and combining the partial structures they represented. Even though this is essentially the same technique they used five months earlier to find latent oxygen atoms in ethers. In several instances, students correctly analyzed a daughter cluster and missed the formula by one Br or Cl atom. Another difficulty for students was the spectra of compounds with four chlorine atoms (e.g., Cl<sub>4</sub>). They are particularly difficult to analyze because of the tiny M + 6 peaks. The inclusion of the section on ultra-tiny peaks and the verification step were added to help students pick the right peak to use as the divisor, even though the peak might be ultra-tiny.

#### **Phase 4**

To test the revised handout, an unplanned fourth phase was added to the study. The revised Handout 2 was given to students to study at home prior to the final laboratory exam during which each student analyzed two spectra. Just prior to executing phase four, students were allowed to view their mistakes from phase three; they were never allowed to take the test spectra home. Two copies each of the 12 spectra that were not correctly analyzed in the basic study were included in the total of 50 spectra in phase four. The spectrum of pentabromophenol was also added to phase four so that a Br<sub>5</sub> compound would be included in the overall study. The results of the 50 spectra analyzed in phase four are shown in the column headed by B in tables 1-3. The students correctly solved for 11 of the 12 values of *n* and *m* they had failed to solve earlier, and they solved the pentabromophenol spectrum. The final overall result of 68 of 69 compounds correctly analyzed for chlorine and bromine suggests that the technique doesn't have a major flaw and can be used by sophomores. The single spectrum that was not correctly analyzed was that of trichloroacetic acid, which displays no molecular-ion cluster. The percentage correct on the three kinds of difficult spectra increased substantially, but these spectra were still difficult for sophomores to interpret. The results are shown in Table 4. In general, students performed better on the more difficult spectra of phase four than they did in phase three. In phase three, they correctly solved only 13 of the 48 (i.e., 27%) difficult spectra. In phase four, they solved 24 of 32 (75%). The improved results suggest the revisions made to Handout 2 were worthwhile. Although students solved 80% of the bromine only spectra, this percentage could be higher. A spectrum such as that of hexabromobenzene causes students problems because peaks at an even *m/z* values are difficult to distinguish from those at odd *m/z* values, and the *m/z* scale contracts significantly with high-mass, multi-bromo compounds. In this study, students were only given written directions. When the chlorine rule is integrated into full structure

determinations, instructors should emphasize that the apparent cluster may be the result of a prior fragmentation. These kinds of spectra are the most difficult for beginners to analyze because of the extra steps involved.

**Table 4 Phase 3 and 4 comparison of spectra by type**

Spectral Type	Phase	Compounds	T	A	B	%
Bromine only	3	12	27	9		33
	4	11	20		16	80
Tiny peaks	3	4	9	3		33
	4	1	3		2	66
Early fragmentation	3	5	12	1		8
	4	4	9		6	67
All Spectra	3	68	150	99		66
	4	20	50		36	72

The results of the four-phase study validate the use of the chlorine rule for sophomore-level mass spectral analysis as judged by the students successfully finding  $n$  and  $m$  for 68 of the 69 compounds in the study. From the instructor's perspective, this month-long experience has sharpened student awareness of  $A + 2$  effects in mass spectra. Even relatively poor students now find it easy to identify chlorine and bromine in  $Br_1$  and  $Cl_1$  compounds. Better students have no trouble finding  $n$  and  $m$  from molecular-ion clusters containing 3-5 peaks, and superior students oft times can propose a constitutional isomer for a structure from the cluster analysis alone. They can also reconstitute fragments to identify the  $Br_mCl_n$  moiety for some spectra.

The guided-inquiry exercise proved useful to students in two ways. When they analyzed real spectra, they had an intuitive feel for the way chlorine dominates clusters because of its 3:1 natural isotopic composition. They also experienced no difficulty finding the number of bromine atoms once the number of chlorine atoms was known. This is attributable to their own derivation of the relationship between  $n$ ,  $m$  and  $M$  in the exercise. The theoretical understanding they gained appeared to help when they started actual spectral analysis. Most students had no trouble finding  $m$  when their value of  $n$  was correct. The overall results of phase four suggest that Handout 2 in its current form can be a useful aid to students in learning what to look for in real spectra.

In brief, students can derive the chlorine rule (Handout 1), and they can use it to find the number of chlorine and bromine atoms in unknown formulas (Handout 2). The findings presented suggest that, with normal instructor interaction in the form of lecture explanations and integrated lab exercises, the chlorine rule can become a practical tool for use in sophomore-level structure determinations. Handouts 1 and 2 are recommended as homework assignments or for use during a laboratory period. Appendix 3 is provided as a summary for cluster-peak analysis. Appendix 4 is an adjunct to the accompanying paper.

## Appendix 1

### Shorthand Procedure for Expanding Binomials

Peak intensities are the coefficients in the polynomial that results upon the expansion of one or more binomials such as  $(a + b)^m$  and  $(3a + b)^n$ . The expansion may be simplified by converting the binomials into isotope patterns (5). The letters  $a$  and  $b$  may be removed along with the plus sign of a binomial, leaving only the coefficients, which are then separated by a colon, as shown below for the bromine and chlorine binomials.

$$(a + b) = (1 \ 1) = 1:1 \quad \text{Br}_1$$

$$(3a + b) = (3 \ 1) = 3:1 \quad \text{Cl}_1$$

The expansions of  $(a + b)^2$  for  $\text{Br}_2$  and  $(3a + b)^2$  for  $\text{Cl}_2$  are shown below.

$$(1:1)(1:1) = 1:2:1 \quad \text{Br}_2$$

$$(3:1)(3:1) = 9:6:1 \quad \text{Cl}_2$$

**Problem:** Find the molecular-ion cluster for  $\text{Br}_2\text{Cl}_2$ . **Solution:** Multiply the two factors.

$$\begin{array}{r} \text{Cl}_2 \quad 9: 6: 1 \quad (1: 2: 1 \quad \text{Br}_2 \\ \quad \quad 18: 12: 2 \\ \quad \quad \quad \underline{9: 6: 1} \\ \text{Br}_2\text{Cl}_2 \quad 9: 24: 22: 8: 1 \quad \underline{\text{Ans.}} \end{array}$$

**Problem:** Find the molecular-ion cluster for  $\text{Br}_3\text{Cl}_3$ . **Solution:** The pattern 9:24:22:8:1 found for  $\text{Br}_2\text{Cl}_2$  is multiplied by 1:1 and 3:1. Because the values of the coefficients increase as  $m$  and  $n$  increase, the likelihood of a mistake is lessened if the 1:1 factor is multiplied last.

$$\begin{array}{r} \text{Br}_2\text{Cl}_2 \quad 9: 24: 22: 8: 1 \quad (\underline{3: 1} \quad \text{Cl}_1 \\ \quad \quad 27: 72: 66: 24: 3 \\ \quad \quad \quad \underline{9: 24: 22: 8: 1} \\ \text{Br}_2\text{Cl}_3 \quad 27: 81: 90: 46: 11: 1 \quad (\underline{1: 1} \quad \text{Br}_1 \\ \quad \quad \quad \underline{27: 81: 90: 46: 11: 1} \\ \text{Br}_3\text{Cl}_3 \quad 27: 108: 171: 136: 57: 12: 1 \quad \underline{\text{Ans.}} \end{array}$$

## Appendix 2

### The Effects of $^{34}\text{S}$ on the Mass Spectra of $\text{Br}_m\text{Cl}_n\text{S}_q$ Compounds

The binomial triad  $(a + b)^m(3a + b)^n(22a + b)^q$  gives the general expression for an ideal  $\text{Br}_m\text{Cl}_n\text{S}_q$  compound. From this expression, the general value of  $I_M$ , the intensity of the lowest-to-highest mass molecular ions, is given by  $1^m 3^n 22^q / 1^m 1^n 1^q = 3^n 22^q$ . This result can be formulated as the ideal equation for the three significant A + 2 atoms in organic structure determinations, as shown in equation 1.

$$I_M = 3^n 22^q \quad (1)$$

Equation 1 predicts  $I_M$  for  $n = 0$  to be  $22^q$  for all values of  $m$ . For 2-bromothiophene, the cluster should be  $(1:1)(22:1) = 22:23:1$ . The mass spectrum of 2-bromothiophene is shown below.

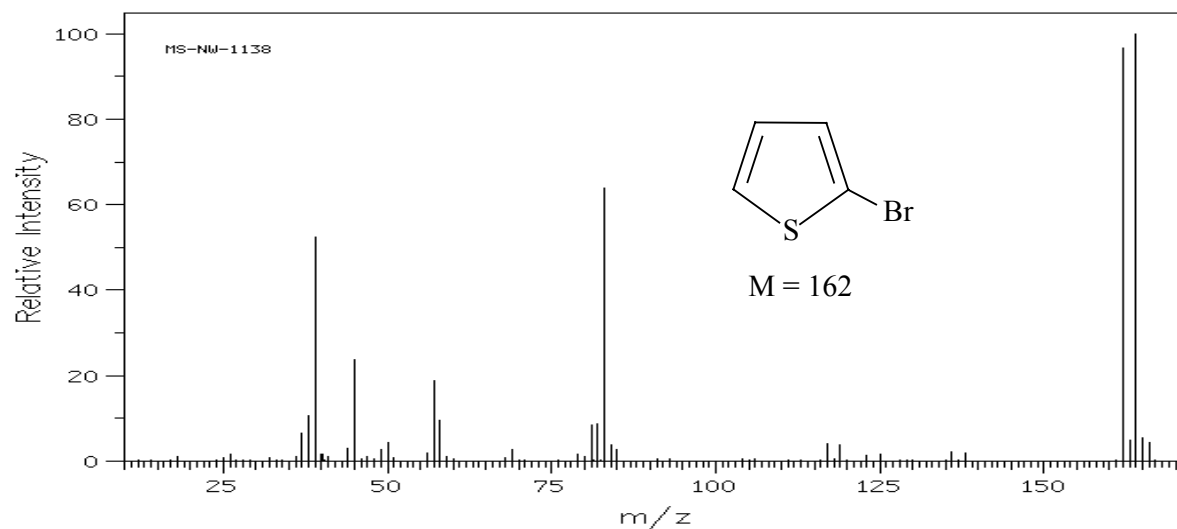


Figure 1. The mass spectrum<sup>8</sup> of 2-bromothiophene reprinted from reference 3.

The actual cluster in the spectrum shows three peaks at  $m/z$  162, 164 and 166 in the ratio 21:21:1. Thus, the peaks at  $m/z$  162 and 164 at 1:1 would signal only  $\text{Br}_1$  if R were taken at  $m/z$  164, but if R is taken at  $m/z$  166, they are 21:21, correctly reflecting the presence of  $\text{Br}_1\text{S}_1$  and the predicted value of  $I_M$  (i.e., 22).

Equation 1 predicts  $I_M$  for  $n = 1$  to be  $(3)(22^q)$  for all values of  $m$ . For 3-chlorothiophene, the cluster should be approximately  $(3:1)(22:1) = 66:25:1$ . The mass spectrum of 3-chlorothiophene is shown below.

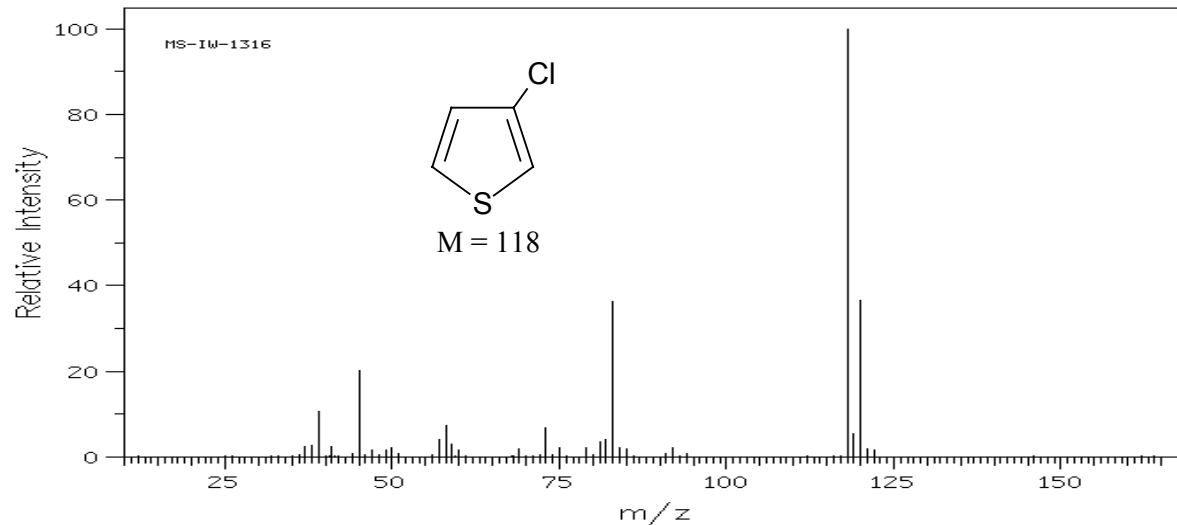


Figure 2. The mass spectrum<sup>8</sup> of 3-chlorothiophene reprinted from reference 3.

The spectrum shows the predicted cluster, three peaks at  $m/z$  118, 120, and 122 in the ratio 66:25:1. Thus, the peaks at  $m/z$  118 and 120 are 3:1 for  $\text{Cl}_1$  if R is taken as  $m/z$  120, but are 66:25, correctly reflecting the presence of  $\text{Cl}_1\text{S}_1$  and the predicted value of  $I_M$  (i.e., 66) if R is taken as  $m/z$  122.

These spectra can be analyzed by finding  $I_M$  by the ratio of  $I_{162}/I_{166}$  for 2-bromothiophene to be near the ideal value of 22, and the ratio  $I_{118}/I_{122}$  for 3-chlorothiophene to be near 66. The  $I_M$  value of 22 is abnormal for chlorine containing compounds (i.e., it is more than the expected 9-12 for  $n = 2$  and less than the expected 27-34 for  $n = 3$ ); the 22 indicates one sulfur atom. Thus, for the compound in Figure 1,  $22 = 3^n 22^q$  for which  $n = 0$  and  $q = 1$ . The three peaks in the cluster are given by  $m + n + q + 1$ ; therefore,  $3 = m + 0 + 1 + 1$  or  $m = 1$ . By this analysis, the spectrum reveals a  $\text{Br}_1\text{S}_1$  compound. Likewise, for the compound of Figure 2, the  $I_M$  value of 66 is abnormal (i.e., it is more than the 27-34 expected for  $n = 3$  and less than the 81-100 expected for  $n = 4$ ). For  $I_M = 66$ ;  $66 = 3^n 22^q$  or  $n = 1$ ,  $q = 1$ ,  $m = 0$ . The spectrum represents a  $\text{Cl}_1\text{S}_1$  compound. These results may be summarized as follows: when  $I_M$  is 22, the compound contains  $\text{S}_1$ ; when  $I_M$  is 66, the compound contains  $\text{Cl}_1\text{S}_1$ . Students who follow the general rule to consider all even mass molecular-ion peaks as part of the cluster will find the correct values of  $I_M$  for  $\text{Br}_m\text{Cl}_1\text{S}_1$  compounds.

Interestingly, were a student to consider only the M and M + 2 peaks in the spectra of 2-bromothiophene and 3-chlorothiophene, the student would find correct values for  $m$  and  $n$ , leaving the presence of sulfur to be identified some other way. The situation would be analogous to the one in which oxygen is a co-heteroatom with bromine and chlorine. In that case, the additional peaks due to oxygen are all too small to observe and the presence

of oxygen must be found in another manner. In most instances, the values found for  $I_M$  by using the penultimate molecular-ion peak in the cluster are below those expected. In general, the values of  $I_M$  for  $Br_mCl_n$  compounds are more than the predicted values of 3, 9, 27, etc. When sulfur is present, the ratio,  $I_M$ , is often outside the expected range of values for  $I_M$  and less than predicted for plain  $Br_mCl_n$  compounds. For 2-bromothiophene (Figure 1),  $I_{162}/I_{164} < 1$ . For 3-chlorothiophene (Figure 2),  $I_{118}/I_{120} < 3$ . Table 1 gives values of  $I_M$  for sulfur containing compounds.

**Table 1.  $I_M$  values for  $Br_mCl_nS_q$  compounds for  $q = 1-4$  sulfur atoms<sup>13</sup>**

$Br_mCl_n$	$C_4-$ $C_{10}$	$C_4S_1-$ $C_{10}S_1$	$C_4S_2-$ $C_{10}S_2$	$C_4S_3-$ $C_{10}S_3$	$C_4S_4-$ $C_{10}S_4$
$Br_1Cl_1$	3- 3	(68) 2.7- (62) 2.6	x(31) 2.3- (28) 2.3	x(19) 1.8- (18) 1.9	x(13) 1.8- (13) 1.7
$Br_2Cl_1$	3- 3	(72) 2.7- (62) 2.6	*(30) 2.2- (28) 2.2	(19) 1.9- (18) 1.8	(13) 1.6- (12) 1.6
$Br_3Cl_1$	3- 3	(64) 2.6- (64) 2.6	*(31) 2.1- (31) 2.1	x(18) 1.7- x(18) 1.7	x(13) 1.5- x(12) 1.4
$Br_1Cl_2$	10- 10	(201) 7.5- (200) 7.2	(98) 5.9 (83) 5.7	(52) 4.8- x(48) 4.6	x(35) 3.9 x(33) 3.8
$Br_2Cl_2$	10- 10	(190) 7.5- (200) 7.2	(94) 5.7- (93) 5.5	(52) 4.5- (46) 4.3	x(33) 3.6 x(32) 3.5
$Br_3Cl_2$	10- 10	(201) 7.4- (200) 7.1	(98) 5.4- (97) 5.2	(47) 4.2- (47) 4.1	*(31) 3.3- (30) 3.3
$Br_1Cl_3$	30- 30	(506) 21- (504) 20	(247) 15- (246) 15	(161) 12 (120) 11	(95) 9.1- (94) 8.7
$Br_2Cl_3$	32- 32	(none) 20- (306) 20	(295) 15- (294) 14	(142) 11- (141) 10	(91) 8.5- (90) 8.2
$Br_3Cl_3$	34- 34	(none) 20 (none) 20	(159) 14- (158) 14	(154) 10- (154) 10	(75) 7.9 (75) 7.5

The values in Table 1 were obtained by analyzing data generated by Yan's isotope-pattern calculator. Consider  $Br_1Cl_1S_2$ . Table 2 shows tabulated intensity values for the molecular ions of  $C_4H_8Br_1Cl_1S_2$ .

**Table 2. Molecular-ion region<sup>2</sup> for  $C_4H_8Br_1Cl_1S_2$**

Mass	Percent
234	72.2
235	4.3
236	100.0
237	6.0
238	31.2
239	1.8
240	2.3
241	0.1
242	0.1

The value of  $I_M = I_{234}/I_{242} = 72.2/0.1 = 722$ , which is indicated by an x in Table 1. The ratio found by  $I_{234}/I_{240} = 72.2/2.3 = 31$ , which is the value in parenthesis in Table 1. The ratio found by  $I_{234}/I_{238} = 72.2/31.2 = 2.3$ , which is posted next to (31) in Table 1. The 2.3 value discounts sulfur ( $q = 2$ ) but indicates its presence by the 2.3

value, which is less than the expected 3+ for  $n = 1$ . The result  $x(31) 2.3$  in Table 1 shows values obtained by dividing the lowest-mass peak successively by  $I_{242}$ ,  $I_{240}$  and  $I_{238}$ . The  $x$  simply means that the value is unreliable because of the small (0.1%) relative intensity of the  $m/z$  242 ion. The  $x(31) 2.3$  result might be recognized as signaling sulfur or the 31 value might be perceived by a student to represent a  $\text{Br}_m\text{Cl}_n$  compound in which  $n = 3$ . An experienced analyst knows that  $\text{Cl}_3$  gives a 27:27:9:1 cluster, which the data in Table 2 cannot support. If a student analyst assumes the  $m/z$  242 intensity is real, then 722 has meaning (i.e., it represents a peak) even though the intensity is too low to quantify the number of S atoms; the model-predicted cluster for  $\text{Br}_1\text{Cl}_1\text{S}_2$  is given by  $(1:1)(3:1)(22:1)^2$  or 1452, 2002, 576, 27, 1. This pattern gives  $x(54) 2.5$ ; this latter number discounts the two sulfur atoms and gives  $n = 1$ . That is, for a real 5-peak cluster  $m + n + q + 1 = 5$ . Discounting  $q = 2$ , the number of peaks becomes  $m + n + 1 = 3$ . The intensities of these three peaks are 1452, 2002, and 576 for which  $1452/576 = 2.5$ . The latter value signals sulfur because it is less than three. The technique of successively dividing by trial R values ultimately leads to an interpretable ratio. This technique will seldom be required, because of the paucity of compounds containing more than one sulfur atom and also halogens.

The spectra of the sulfur containing compounds listed in Table 3 might be amenable to sophomore-level analysis. Sulfur was not included in the study described in this supplement.

**Table 3.  $\text{Br}_m\text{Cl}_n$  compounds containing one sulfur atom**

$\text{Br}_m\text{Cl}_n$	Name	CAS Registry Number	SDBS No.	Spec. No.
$\text{Br}_1$	2-bromo-5-methylthiophene	765-58-2	155	4174
$\text{Br}_1$	2-bromothiophene	1003-09-4	4140	1138
$\text{Cl}_1$	3-chlorothiophene	17249-80-8	5333	1316
$\text{Cl}_1$	2-chlorothiophene	96-43-5	476	1141
$\text{Cl}_1$	<i>p</i> -chlorobenzenethiol	106-54-7	4452	3102
$\text{Cl}_1$	(2-chloroethylthio)benzene	5535-49-9	19493	7364
$\text{Cl}_1$	<i>o</i> -chloro- $\alpha$ -toluenethiol	17733-22-1	21757	1509
$\text{Br}_1\text{Cl}_1$	<i>o</i> -chlorobenzenethiol	6320-03-2	23272	9725

## Appendix 2 Conclusions

Though it has not been demonstrated by student analyses, first-year organic students should be able to handle  $\text{Br}_m\text{Cl}_1\text{S}_1$  compounds (i.e., those that contain a maximum of one each sulfur and chlorine atoms). More complex formulas involving sulfur and silicon are best avoided at the introductory level.

### Appendix 3

#### General Considerations for Molecular-Ion Analyses

One way to evaluate molecular-ion regions of mass spectra is to sort them by the number of visible cluster peaks and by the cluster's symmetry in the spectrum. So doing, leads to the following summary for the most commonly encountered problems in organic structure determinations (i.e.,  $M$  equals four or fewer peaks).

1. **One-peak molecular ion ( $M = 1$ ):** Sample contains no Cl, Br, S, or Si.

2. **Two-peak clusters ( $M = 2$ ):**

a. Symmetric: 1:1 (twin towers) = Br<sub>1</sub>

b. Asymmetric: 3:1 = Cl<sub>1</sub>, 22:1 = S<sub>1</sub>, 30:1 = Si<sub>1</sub>

3. **Three-peak clusters ( $M = 3$ ):**

a. Symmetric: 1:2:1 (spire) = Br<sub>2</sub>;

b. Asymmetric

1. Down-slope clusters (second peak less intense than first): Sample contains no Br; 9:6:1 = Cl<sub>2</sub>, 66:25:1 = Cl<sub>1</sub>S<sub>1</sub>, 90:33:1 = Cl<sub>1</sub>Si<sub>1</sub>;

2. Up-slope clusters (second peak more intense than first): Sample contains Br; 3:4:1 = Br<sub>1</sub>Cl<sub>1</sub>; 22:23:1 = Br<sub>1</sub>S<sub>1</sub>; 30:31:1 = Br<sub>1</sub>Si<sub>1</sub>.

4. **Four-peak clusters ( $M = 4$ ):**

a. Symmetric: 1:3:3:1 (twin towers) = Br<sub>3</sub>;

b. Asymmetric: Contains Cl: 3:7:5:1 = Br<sub>2</sub>Cl<sub>1</sub>; 9:15:7:1 = Br<sub>1</sub>Cl<sub>2</sub>; 27:27:9:1 = Cl<sub>3</sub>; 66:91:26:1 = Br<sub>1</sub>Cl<sub>1</sub>S<sub>1</sub>.

The lead number in each pattern tells all! 3 = Cl<sub>1</sub>; 9 = Cl<sub>2</sub>; 22 = S<sub>1</sub>; 27 = Cl<sub>3</sub>; 30 = Si<sub>1</sub>; 66 = Cl<sub>1</sub>S<sub>1</sub>; 81 = Cl<sub>4</sub>; 90 = Cl<sub>1</sub>Si<sub>1</sub>. All that is needed is the set of relative abundances for A + 2 elements: Cl = 3:1, Br = 1:1, S = 22:1, and Si = 30:1.

## Appendix 4

### The Effects of $^{13}\text{C}$ and $^2\text{H}$ on the Mass Spectra of $\text{Br}_m\text{Cl}_n$ Compounds

Equation 1 is derived from the binomial pair  $(a + b)^m(3a + b)^n$  as shown in the accompanying paper.

$$I_M = 3^n \quad (1)$$

The binomial pair may be rewritten in terms of the actual isotopic ratios of bromine and chlorine (6) as  $(1.028a + b)^m(3.129a + b)^n$ . The coefficient of the first term of the general expansion of this new binomial pair is  $(1.028^m)(3.129^n)$ , which gives the normalized intensity  $I_M$  for  $\text{Br}_m\text{Cl}_n$  compounds less the contribution of the hydrocarbon residue as shown in eq 2.

$$I_M = (1.028^m)(3.129^n) \quad (2)$$

Table 1 shows  $I_M$  as given by eq 1, by eq 2, and by normalized computer-generated data for the nine  $\text{C}_{10}\text{H}_{22-m-n}\text{Br}_m\text{Cl}_n$  formulas (see Figure 3 of the paper for the clusters). The model-generated intensities of eq 1 are shown in column two. They may be compared to the intensities in column three, which are obtained by eq 2, or to those in the last column, which are the computer-generated  $I_M$  intensities of the corresponding decanoids. The eq 2 values are equivalent to Beynon's calculations, but are rounded to whole numbers.

**Table 2. Normalized intensity values  $I_M$  for  $\text{Br}_m\text{Cl}_n$  Compounds**

$\text{Br}_m\text{Cl}_n$	Equation 1 $3^n$	Equation 2 $(1.028)^m(3.129)^n$	Decane derivatives
$\text{Br}_1\text{Cl}_1$	3	3	3
$\text{Br}_2\text{Cl}_1$	3	3	3
$\text{Br}_3\text{Cl}_1$	3	3	3
$\text{Br}_1\text{Cl}_2$	9	10	10
$\text{Br}_2\text{Cl}_2$	9	10	10
$\text{Br}_3\text{Cl}_2$	9	11	10
$\text{Br}_1\text{Cl}_3$	27	31	30
$\text{Br}_2\text{Cl}_3$	27	32	32
$\text{Br}_3\text{Cl}_3$	27	33	34

The eq 1 values of  $I_M$  in Table 2 are close enough to real cluster values that the model gives the correct value of  $n$  when eq 1 is solved for the  $I_M$  values of real compounds. The notion that carbon and hydrogen isotope effects may be ignored for  $\text{C}_{10}$  compounds is validated for compounds typically encountered in a sophomore-level course. Consider  $\text{C}_{10}\text{H}_{16}\text{Br}_3\text{Cl}_3$ , a  $\text{Br}_3\text{Cl}_3$  compound for which  $I_M$  is 34 as shown in Table 2. To find  $n$  mathematically by eq 1,  $I_M = 3^n$  or  $34 = 3^n$ . The solution for  $n$  is 3.2, but  $n$  must be a whole number; therefore,  $n = 3$ . Thus, the number of chlorine atoms in  $\text{C}_{10}\text{H}_{16}\text{Br}_3\text{Cl}_3$  may be found directly from  $I_M$ . Likewise, the application of eq 1 to the other computer-generated values of  $I_M$  gives the correct value of  $n$ . In practice, it is not necessary to solve

for  $n$  mathematically. It is merely necessary to compare the normalized value of  $I_M$  to the nearest allowed value of  $I_M$  as predicted by the model. These values are 1, 3, 9, 27, 81, ...,  $3^n$ . An  $I_M$  value of 34 is much closer to 27 than it is to 81, so for  $I_M = 34$ ,  $n = 3$ . Real intensities rise approximately as 1, 3, 10, 30, 100, 300, etc. Thus, the lead numbers in both model-produced and computer-produced clusters in Figure 3 reveal stoichiometry when the cluster is normalized. Note, a cluster must be normalized before the stoichiometry is apparent. Thus, when the clusters are normalized; the first term in each set of numbers uniquely defines  $n$  for a given cluster. When the lead number of a cluster is near model-allowed values of 3, 9, or 27, then  $n$  is 1, 2, or 3, respectively. The chlorine rule is thus empirically educible from the normalized ideal clusters shown in Figure 3 of the paper.

The clusters of ideal compounds that contain both bromine and chlorine may now be rationalized in the following manner. The effect on an ideal cluster of the addition of bromine is to increase the number of peaks in the cluster by one but to have no effect on the intensity of the end peaks. The effect on an ideal cluster of the addition of chlorine is to increase the number of peaks in the cluster by one and to increase the intensity of the lowest-mass ion  $M$  by a factor of three for each chlorine atom added. The addition of either halogen causes an increase in the intensities of the interior peaks. For a normalized cluster, the number of chlorine atoms in the underlying compound is determined solely by the magnitude of the intensity of the lowest-mass ion in the cluster. When  $I_M = 1, 3, 9, 27, 81$ , etc.,  $n = 0, 1, 2, 3, 4$ , etc. These findings can be applied to real clusters, because the discrete nature of chlorine atoms requires  $n$  to be a whole number.

## Instructor Notes

1. The figures and tables in each independent section (e.g., the handouts and appendixes) are numbered independently, so they may be copied and used independently.
2. All computer-generated molecular-ion data in this supplement were obtained from the web site found in reference 1 with the permission of Junhua Yan who developed the isotope pattern calculator.
3. The web site shows students how to use Excel to prepare a histogram. The site is part of LabWrite 2000, developed at the North Carolina State University (Mike Carter, Principal Investigator).
4. Appendix 1 shows a shorthand procedure for the expansion of binomials.
5. Solutions are deleted prior to student use of the handouts.
6. Appendix 2 shows the isotope effect of sulfur in  $\text{Br}_m\text{Cl}_n\text{S}_q$  compounds. Sulfur containing compounds were not part of the original study and were not included in student unknowns.
7. The use of the intensity of the  $R - 2$  mass ion discounts the presence of one sulfur atom in the formula.
8. The mass spectra in this study were downloaded free from the mass spectral section of the Integrated Spectral Data Base System for Organic Compounds (SDBS) at the web site, reference 3, of the National Institute of Advanced Industrial Science and Technology in Tsukuba, Ibaraki, Japan. This data base is maintained under the direction of N. Wasada. The SDBS numbers are that site's internal reference numbers, and the corresponding mass spectrum number is found in the upper left corner of the spectrum. For example, the SDBS number for bromodichloromethane is 5235 and its mass spectrum number is 2956 as seen in Figure 3 of Handout 2.
9. The value of  $M$  was provided for 5 compounds.
10. None of the unknown compounds have more than one nitrogen atom in their formula. By the nitrogen rule, an odd-mass  $M$  ion indicates the presence of an odd number of nitrogen atoms.
11. The focus of this study is the molecular-ion cluster not the full mass spectrum. Students who participated in this study are normally expected to find the presence of an aldehyde group by companion IR and  $^1\text{H}$  NMR analyses, but advanced students should be able to deduce this information from the mass spectrum.
12. An asterisk next to the name of a compound in Tables 1 and 2 indicate that the value of  $M$  for that compound is indicated on the spectrum, because  $M$  is not readily discernible from the spectrum.
13. The asterisks in Table 1 of Appendix 2 indicate  $\text{Br}_m\text{Cl}_n\text{S}_q$  formulas that give  $I_M$  values that might be confused with an observed value of  $I_M$  for a  $\text{Br}_m\text{Cl}_n$  compound.

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