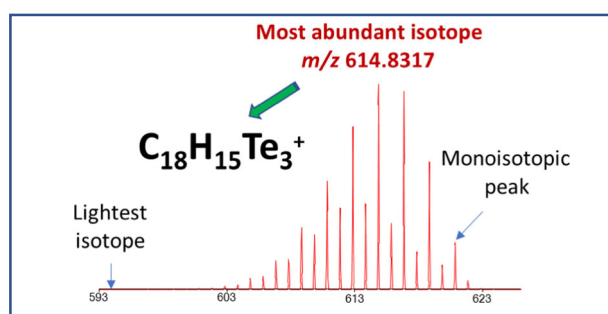


Elemental Composition Determinations Using the Abundant Isotope

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Abstract. Elemental compositions are commonly determined from the exact m/z of the monoisotopic peak, which is often the lightest isotope. However, the lightest isotope peak is often weak or absent and the monoisotopic peak can be difficult to identify for organometallics, polyhalogenated compounds, or large molecules. An alternative approach using the abundant isotope for elemental composition determinations is presented here.

Keywords: Elemental compositions, Software, Organometallic, Halogenated, Isotope

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Introduction

The exact mass of the monoisotopic peak is commonly used to determine candidate elemental compositions by finding all combinations of specified elements that have a calculated monoisotopic mass [1] within user-defined constraints (unsaturation and even- or odd-electron ion type) and a specified error tolerance [2–4]. The monoisotopic peak is generated from the most abundant isotope of each element, and it is only the lightest isotope for simple organics with fewer than approximately 90 carbons. For large, polyhalogenated, or organometallic compounds, the lightest isotope is often weak or absent, and the monoisotopic peak may not be easily recognized. In such cases, it may be preferable to calculate candidate elemental compositions from the abundant isotope.

Experimental

Positive-ion mass spectra were measured with a high-resolution time-of-flight mass spectrometer (AccuTOF-

DART, JEOL USA, Inc., Peabody, MA, USA) equipped with a direct analysis in real time (DART) ion source [5] (DART-SVP, IonSense LLC, Saugus, MA, USA). Helium gas was used with the DART gas heater set to 350 °C and the DART exit electrode set to +150 V. The mass spectrometer conditions were as follows: resolving power = 10,000 (FWHM), orifice 1 = 20 V, orifice 2 = 5 V, ring lens = 5 V, RF ion guide potential = 600 V, and spectral acquisition rate = 1 spectrum s^{-1} for the m/z range 70–1000. Diphenyl ditelluride (98%) was obtained from Sigma Aldrich (St. Louis, MO). Samples were measured by touching the sealed end of a disposable melting point tube to the neat sample and dangling the sealed end of the tube in the DART gas stream approximately 1 mm in front of the exit of the DART source. A mass spectrum of Jeffamine® M-600 (Huntsman Corporation, The Woodlands, TX, USA) was measured as an external reference standard for exact mass measurements [6, 7].

A function was added to the *Mass Mountaineer*TM (massmountaineer.com) program to calculate elemental compositions from the exact mass of the abundant isotope. The calculation is a simple variation of the traditional algorithm for calculating candidate elemental compositions from the measured monoisotopic mass. For each combination of elements, the theoretical isotope distribution is calculated. If the mass difference between

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the theoretical abundant isotope mass and the measured abundant isotope mass is within the specified error tolerance, the candidate composition checked to see if its unsaturation and ion type are within limits. All candidate compositions that are within limits are reported.

The candidate compositions can be further filtered in an optional second step by matching the calculated isotope distributions for each composition against the measured isotope distributions [8–13]. The standard isotope matching function in *Mass Mountaineer* was used without modification. An isotope matching score is calculated as the scaled product of the root-mean-square (rms) deviation between calculated and measured masses (Δm) multiplied by the rms deviation between the calculated and measured isotope abundances (Δa), divided by the number of isotope peaks (n_i) found within specified mass and abundance tolerances.

$$\text{score} = 100.0 \times \Delta m \times \Delta a / n_i$$

The lowest score is the best isotope match with a score of zero denoting a perfect match.

Results and Discussion

Diphenyl ditelluride was chosen as an example of a compound with a complex isotope pattern. Tellurium has eight stable isotopes with masses ranging from 119.9040 (0.2640% relative abundance) to 129.9062 (100.0% relative abundance). Figure 1 shows the positive-ion DART mass spectrum of diphenyl ditelluride. The calculated isotope pattern for $(C_6H_5Te)_2^{++}$ has 22 isotope peaks with the lowest- m/z isotope at m/z 395.8853 having a relative abundance of only 0.0190% relative to the abundant isotope at m/z 409.8877 (relative abundance 100%). The monoisotopic peak occurs at m/z 413.8907. The measured abundant isotope of the molecular ion $(C_6H_5Te)_2^{++}$ is observed at m/z 409.8889, a difference of +1.2 mmu from the calculated value. An unassigned adduct appears with the abundant isotope at m/z 614.8342 comprising the base peak for this mass spectrum. Isotope clusters are observed at lower intensity with abundant isotope at m/z 332.8510, 426.909, 630.829, and 646.8246.

Table 1 shows the elemental composition assignments for the labeled peaks in Figure 1 using the abundant isotope,

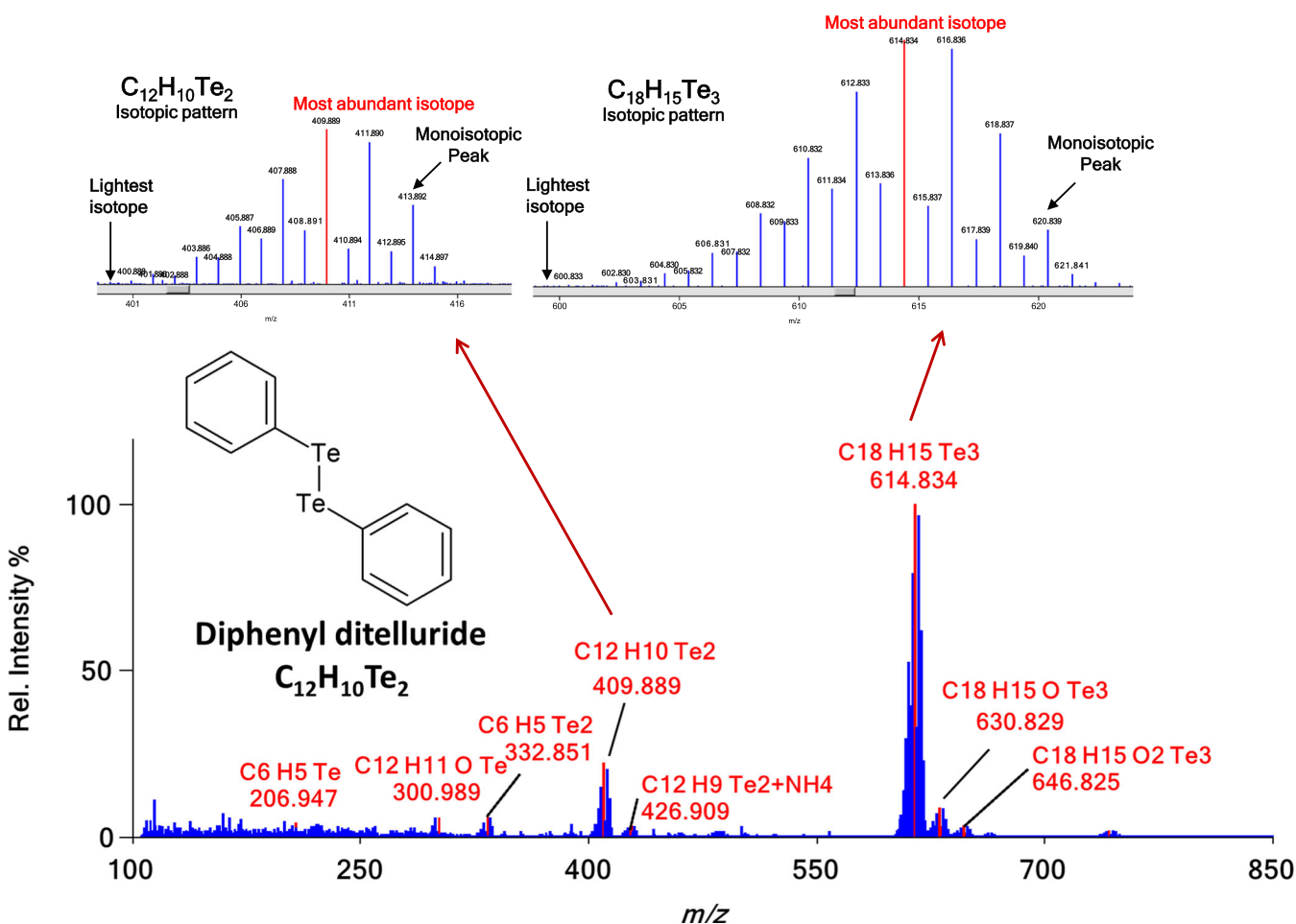


Figure 1. Positive-ion DART mass spectrum of diphenyl ditelluride

Table 1. Elemental Compositions Calculated Using the Abundant Isotopes

Calc. m/z	Abund %	mmu ^a	DBE ^b	Composition	Assignment
332.848459	6.153	-2.55	6.5	C ₆ H ₅ Te ₂	[M - C ₆ H ₅] ⁺
409.887668	22.176	-1.22	10.0	C ₁₂ H ₁₀ Te ₂	M ⁺
427.922042	3.440	0.84	8.5	C ₁₂ H ₁₄ N ₁ Te ₂	[M + NH ₄] ⁺
614.831695	100.000	-2.53	14.5	C ₁₈ H ₁₅ Te ₃	[M + C ₆ H ₅ Te] ⁺
630.826616	8.700	-2.61	14.5	C ₁₈ H ₁₅ O ₁ Te ₃	[M + C ₆ H ₅ Te + O] ⁺
646.821537	3.209	-3.05	14.5	C ₁₈ H ₁₅ O ₂ Te ₃	[M + C ₆ H ₅ Te + O ₂] ⁺

^aMass difference in mmu^bDouble bond equivalents

a 5-mmu mass tolerance, both even- and odd-electron ion types, and element limits C₀₋₂₀H₀₋₅₀O₀₋₁₀N₀₋₁₀Te₀₋₄. These limits take into account the DART positive-ion mechanism involving reactions with atmospheric water and the possibility of observing ammonium adducts in positive ion DART.

Table 1 only shows the most probable assignments for each peak. Complete tables including all of the candidate compositions for each peak are included in the [Supporting Material](#). The composition assignments labeled in Figure 1 are supported by isotope matching. The effectiveness of isotope matching can be shown for the molecular ion isotope cluster. There are 12 possible compositions for a 5-mmu error tolerance and element limits C₀₋₂₀H₀₋₅₀O₀₋₁₀N₀₋₁₀Te₀₋₄. Isotope matching reduces the number of compositions to 6, with the best match being the correct composition (Table 2). The program also identifies one compound with the best-match composition in the NIST 2017 Mass Spectral Database (<http://chemdata.nist.gov>). This is the correct compound: diphenyl ditelluride. Isotope matching retains the most probable composition in all cases and scores this composition as the best match for all species except m/z 630.8292 and m/z 646.8246 which overlap other isotope distributions and have the 7th and 5th best isotope match score, respectively.

An alternate approach to assigning elemental compositions for the C₁₈H₁₅Te₃ isotope cluster is to “guess” at the monoisotopic peak and to use isotope matching to evaluate each result. While this approach (illustrated for the C₁₈H₁₅Te₃ isotope cluster in the [Supporting Material](#)) is successful in this case, it is tedious and may fail for complex isotopic compositions. As an example, the molecular ion of

the flame retardant decabromodiphenyl ether (C₁₂BrO) has a monoisotopic peak at m/z 949.1783 with an abundance of only 0.45% relative to 100% for the abundant isotope at m/z 959.1681. Because interferences or a poor signal-to-noise may hinder the observation of the monoisotopic peak, it is preferable to determine the elemental composition from the abundant isotope.

Conclusion

Elemental compositions can be determined from the abundant isotope. The calculation is more computationally intensive and therefore slower than traditional calculations using the monoisotopic peak. For the examples in this paper, the calculation was approximately 5–10 times slower than calculations using the monoisotopic peak, but the calculation time was still less than 10 s on a laptop computer. Despite the increase in computation time, this provides a method for assigning compositions for species with complex isotope patterns for which the monoisotopic peak is weak, absent, or difficult to determine.

A limitation of this approach is the case of overlapping isotopic distributions, such as M⁺ and [M + H]⁺. An elemental composition can be calculated from the abundant isotope for either species. However, if the overlap results in an abundant isotope that is not the same nominal m/z as the abundant isotope for either molecular ion or protonated molecule, then there is not a clear approach to determining the elemental composition. Isotope matching for overlapping distributions presents additional problems that are beyond the scope of this Application Note.

Table 2. Isotope Matching Results for the Peaks with Measured Abundant Isotope at m/z 409.88889

Calc. m/z	Abund %	mmu ^a	Peaks ^b	Score ^c	DBE ^d	Composition	NIST ^e
409.887668	0.93	0.54	18	0.002762	10.0	C₁₂H₁₀Te₂	1
409.890717	1.83	0.79	18	0.008074	2.0	C ₁ H ₁₀ O ₃ N ₆ Te ₂	0
409.892093	1.72	1.31	18	0.012578	1.5	C ₃ H ₁₂ O ₄ N ₃ Te ₂	0
409.893415	1.49	1.85	18	0.015258	6.5	C ₄ H ₈ N ₇ Te ₂	0
409.893470	1.62	1.89	18	0.017006	1.0	C ₅ H ₁₄ O ₅ Te ₂	0
409.889109	23.68	0.86	13	0.157331	12.0	C ₇ O ₇ N ₆ Te ₁	0

^aRoot-mean-square deviation between measured and calculated isotopes^bNumber of measured peaks corresponding to isotopes calculated for each composition^cComposite isotope matching score for each composition (see text for an explanation)^dDouble bond equivalents for each composition^eNumber of compounds listed in the NIST 2017 Mass Spectral Database for this composition

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