Collision induced dissociation mass spectrometry challenge

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We would like to invite you to participate in the Analytical Challenge, a series of puzzles to entertain and challenge our readers. This special feature of “Analytical and Bioanalytical Chemistry” has established itself as a truly unique quiz series, with a new scientific puzzle published every other month. Readers can access the complete collection of published problems with their solutions on the ABC homepage at <http://www.springer.com/abc>. Test your knowledge and tease your wits in diverse areas of analytical and bioanalytical chemistry by viewing this collection.

In the present challenge, mass spectrometry is the topic. And please note that there is a prize to be won (a Springer book of your choice up to a value of €100). Please read on...

Meet the challenge

Atmospheric pressure ionization techniques allow for the hyphenation of liquid chromatography separations with mass spectrometry and enable the sensitive and selective analysis of non-volatile and thermally labile substances in complex biological and environmental samples. Structural information from ions generated by these “soft” ionization techniques is usually obtained through ion fragmentation by collision induced dissociation (CID). Compared with mass spectra from

electron impact ionization typically used in GC-MS, CID spectra are generally considered less reproducible and less suitable for database searching. Non-target approaches in the fields of metabolomics, environmental, and food analysis use LC-MS methods designed to detect thousands of sample components along with statistical approaches to determine the presence of analytes of significance. Identification of these components is usually carried out by database search, retention time and spectral matching against authentic standards, or manual data interpretation as a last resort. This type of de novo identification of unknown compounds from mass spectrometry data, when no standards are available, remains a significant challenge and a limit to throughput in these fields. In many cases, tandem mass spectrometry can provide rich structural data that enables tentative identification of unknown compounds, but other times MS/MS is only able to provide information about a compound class or some functional groups present.

It is important to fully understand the chemical processes that occur in CID in order to be able to extract the most structural information possible from the mass spectra of unknown compounds. Some reactions observed in CID can be linked to specific structural features of a molecule. In some cases, unusual neutral mass losses or gains (not explained by loss of typical neutral molecules) are observed in CID, providing a great deal of structural information.

The challenge

Figures 1, 2, 3 and 4 show CID spectra of four unrelated compounds all analyzed on an ion trap mass spectrometer using either positive or negative electrospray ionization. In all four cases, product ions with unusual mass shifts to m/z values higher than that of the selected precursor are detected.

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Fig. 1 Collision induced dissociation spectrum of protonated guanine selected at m/z 152

Figure 1 shows the CID spectrum of the protonated nucleobase guanine (m/z 152.1), where an unexpected peak of 1 Da above the precursor is detected at m/z 153. Figure 2 shows the CID spectrum of deprotonated dodecanedioic acid at m/z 229, a metabolic intermediate and urinary biomarker showing a mass increase of 14 Da for its CID product detected at m/z 243. Figure 3 shows the CID spectrum of protonated 3-formylchromone, a plant metabolite. This spectrum shows a peak at 16 Da above the precursor selected in MS^2 at m/z 175. Finally, Fig. 4 shows the CID spectra of folic acid in positive ionization mode including the MS^2 spectrum of the vitamin (m/z 442 in Fig. 4a) and that of its glutamic acid loss product ion isolated in MS^3 (m/z 295 in Fig. 4b). In this case, the m/z 313 product ion in MS^2 and MS^3 (Fig. 4a) originates from the mass increase of 18 Da with respect to the m/z 295 product ion rather than from the protonated folic acid precursor.

Based on the structures and spectra provided, your task is to explain the unusual mass gains (+1 Da, +14 Da, +16 Da, and +18 Da) observed in CID spectra of these selected compounds and to determine the common ionic structural feature

Fig. 2 CID spectrum of deprotonated dodecanedioic acid with precursor ion of m/z 229.1

Fig. 3 CID spectrum of protonated 3-formylchromone with precursor ion of m/z 175 selected in MS^2

that leads to all these unusual mass products. Finally, propose a reaction mechanism that could occur in both positive and negative ionization mode to give these unique products.

Fig. 4 a CID spectrum of protonated folic acid in MS^2 showing elimination of glutamic acid (Glu) detected at m/z 295 and b MS^3 spectrum of the m/z 295 product ion

We invite our readers to participate in the Analytical Challenge by solving the puzzle above. Please send the correct solution to abc-challenge@springer.com by March 1, 2018. Make sure you enter “Collision induced dissociation mass spectrometry challenge” in the subject line of your e-mail. The winner will be notified by e-mail and his/her name will be published on the “Analytical and Bioanalytical Chemistry” homepage at <http://www.springer.com/abc> and

in the journal (volume 410/issue17) where readers will find the solution and a short explanation.

The next Analytical Challenge will be published in 410/10, April 2018. If you have enjoyed solving this Analytical Challenge you are invited to try the previous puzzles on the ABC homepage.