Identification of Polyethylene Glycol Based Surfactants Using LC-MS Data

It can be difficult to identify PEG (polyethylene glycol) based surfactants by mass spectrometry. One needs to determine the end group on the chain. We employ two different approaches. The first uses nominal molecular weight data and the other uses accurate mass data. Nevertheless, both require one to obtain a list of candidate structures for consideration by using Excel spreadsheets of tabulated components. The candidates from the spreadsheet are then narrowed using either in-source or tandem (MS/MS) collisionally induced dissociation data or other information.

Nominal MW Using Residual Molecular Weight: The nominal molecular weight method utilizes a residual molecular weight (RMW) calculation. One can choose any of the species in the PEG distribution for the calculation of this RMW index. *All the PEG oligomeric species in a series have the same RMW.* The calculations are based on the neutral mass so all the ion adducts for the cations are removed or the observed anions corrected for the loss of a proton or ion adducts before calculating this index \[6,7\].

Some data systems such as Water’s MassLynx do not correct for the mass of an electron and will give a bias (~0.0005 m/z units) in the calculations \[4,5\]. All the values in the following calculations do correct for the mass of an electron.

For example, if one is attempting to identify a nonionic surfactant, pick one of the ammonium adduct ions for the PEG series. For example, the ammonium adduct was noted at a nominal mass of 820.6. Thus the neutral mass for the PEG nonionic surfactant species would be m/z 802. Be sure to change the observed mass to its nominal mass. Be aware of the nominal mass being increased by the data system as the number of hydrogens in the molecule increases!

Ammonium adduct m/z 820.6
Neutral species m/z 802.6
Nominal molecular weight 802

Residual Molecular Weight = RMW = \((x/44)-y\)44

\(x\)=the observed nominal molecular weight of the surfactant species
\(y\)=integer value for \(x/44\), i.e. the whole number to the left of the decimal

RMW =\((802/44)-y\)44 = \((18.227)-y\)44 = \((18.227)-18\)44 = (0.227) 44 = 9.99 = 10

Sort the spreadsheet of literature or TSCA PEG surfactants values by RMW and find the candidates with a RMW of 10. There were several possibilities, but using MS/MS or insource collisionally induced dissociation data, the nonionic surfactant can be identified as a C12 terminated PEG nonionic surfactant.
Accurate Mass Data Using Kendrick Mass Defect: Fewer candidates will be obtained when the accurate mass data is employed with Kendrick mass defect [1-3] indices. The accurate mass data should preferably have an error less than 5 ppm. The calculations are based on the neutral mass so all the ion adducts for the cations are removed or the observed anions corrected for the loss of a proton or ion adducts before calculating the index [6,7].

Some data systems such as the Waters MassLynx do not correct for the mass of an electron in their data system [4,5]. This will give a slight bias (~0.0005 m/z units) in the measurement. All the values in the following calculations do correct for the mass of an electron.

As before, any species in the PEG series for the nonionic surfactant is chosen. All the PEG oligomeric species in a series have the same Kendrick mass defect index. The accurate mass for the ammonium species is shown below:

Accurate mass for ammonium ion m/z 820.59920
Accurate mass for neutral species 802.56537

Kendrick mass = (monoisotopic mass) (44/44.02621) = (802.56537) (0.9994046) = 802.08752

Kendrick mass defect = nominal Kendrick Mass – Kendrick Mass = 802 – 802.08752 = -0.08752

Sort the spreadsheet of literature or TSCA PEG surfactants values by Kendrick mass defect and find the candidates with a MW near -0.08752. In the “Literature-Real” section of the spreadsheet, there was only one candidate found, the C12 terminated PEG nonionic surfactant. Again, the structure could easily be confirmed by interpretation of either its MS/MS spectrum or insource collisionally induced dissociation spectrum.

C12 terminated PEG Nonionic Surfactant
RMW = 10

Kendrick Mass Defect = -0.08752
References


7. List of Ion Adducts Calculated with ChemDraw Ultra below by J. Little:

<table>
<thead>
<tr>
<th>Ion Adduct</th>
<th>m/z value</th>
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<tbody>
<tr>
<td>ammonium</td>
<td>18.03383</td>
</tr>
<tr>
<td>potassium</td>
<td>38.96316</td>
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<tr>
<td>sodium</td>
<td>22.98922</td>
</tr>
<tr>
<td>protonated</td>
<td>1.00728</td>
</tr>
<tr>
<td>deprotonated</td>
<td>-1.00728</td>
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<tr>
<td>chloride</td>
<td>34.9694</td>
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<tr>
<td>acetate</td>
<td>59.01385</td>
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<tr>
<td>formate</td>
<td>44.9982</td>
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