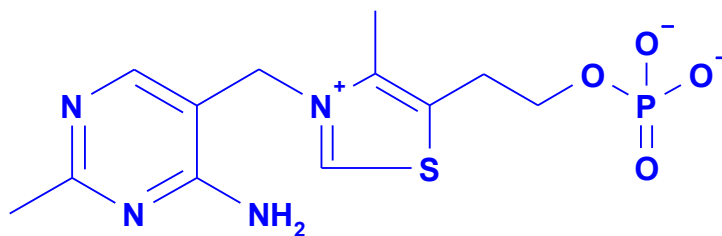


A May 2008 paper in JASMS (Manier et.al.) discussed some common background contaminants in lipid analyses. The spectrum of thiamine monophosphate in negative ion mode shows some subtle problems with adducts that also sometimes arise. I am referring here to spectrum KO006278 in the very interesting MassBank (<http://www.massbank.jp>).



Molecular Formula =C₁₂H₁₆N₄O₄PS

For purposes of illustration,. I have removed all fragment ions less than 3% intensity, because most of these ions are noise. The following spectrum list remains:

Mass	Intensity
96.9672	398.000
171.1385	35.000
221.9987	100.000
245.0836	429.000
264.1581	32.000
283.2653	140.000
343.0387	78.000
343.0634	117.000

The fairly large 283 fragment ion in this 10V negative ion spectrum was perplexing. The mass loss from the parent ion was 60 daltons which appears difficult to get from this structure without some major rearranging of heavy atoms. The smaller 171 and 264 ions are also difficult to explain, based on the structure.

The 283 ion is probably stearate anion. Like dioctyl phthalate, the fatty acids stearic and palmitic acid are frequently present in LCMS mobile phases. In negative ion mode, if ammonium acetate is present in the mobile phase, many compounds will give acetate adducts (at M + 59). Stearic acid has a molecular weight of 284 and so its adduct will have a mass of 343; by chance the negative ion of thiamine phosphate has the same mass. Thus the daughter ion spectrum observed here is really the combined spectrum of both thiamine monophosphate and the acetate adduct of stearic acid. The mass defect of the observed 283 ion is about 5ppm different than the theoretical defect of stearate anion; there was also a very small 59 ion which is probably acetate anion.

Moreover, the 171 ion is probably due to capric acid (decanoic acid). Capric acid has a molecular weight of 172. Like acetate, it can form adducts. The adduct that is observed is the adduct of itself (dimer) to form a (172 + 171) 343 ion. The mass defect of the caprate anion is an exact (0 ppm) match for the observed 171 anion. KO006278 is quite probably three structures in one spectrum

The eight data points above were saved in file neg1. The isotopic data (filename ineg) was computer generated, as no isotopic data was available. The IndexSearch results thus obtained can be viewed with the link here. <http://www.mathspec.com/thiamin.html>