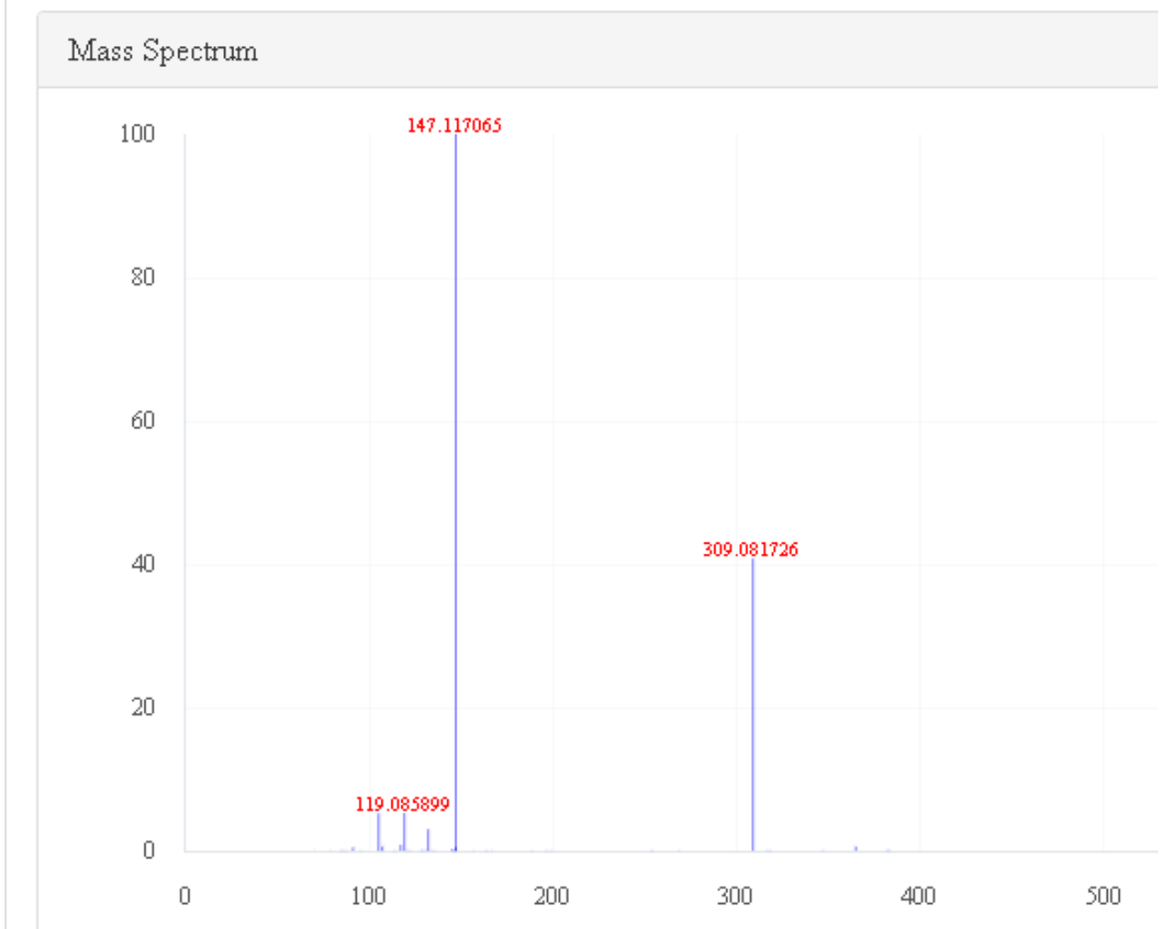
Recently, I was looking at two MS/MS spectra (high and low CE pair) from an environmental sample. Our MathSpec SPS did not suggest any suspect compounds for these two spectra, but the two spectra are sodium adducts which are usually difficult to identify. Our SPS accurate-mass link to the EPA CompTox Chemicals Dashboard indicated that propargite was the only QC level 1 compound with a similar exact mass. Looking up propargite (CID4936) in PubChem, I was pleased to see that Pubchem Compound has accurate-mass fragmentation spectra of both protonated propargite and the sodium cation adduct of propargite. However, based on these spectra, one could eliminate propargite – but do look closely at the spectra. The spectrum of the protonated adduct is shown below. The MS/MS header is on the next page.

I was surprised to see in the library spectrum that the protonated precursor ion has a mass of 365.145 Da while the compound has an exact mass of 350.1552 Da - which fits the formula of C19H26O4S. The precursor of the sodiated adduct was at 387.127, not 373 Da. I stumble upon these contradictions occasionally. I am curious and so I usually try to identify the compound that goes with the spectrum. I believe that this spectrum is a spectrum of pyridaben, Pubchem 91754 (364.1376 Da), although it would also be difficult to miss a chlorine isotope in the full ms1 spectrum.

SPLASH: splash10-0002-0903000000-9bb4b3785052b2ed5770 Submitter: GNPS Team



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When the chemist generated this new reference spectrum for GNPS, why was he or she not curious about the obvious mass discrepancy of 14 Da and the presence of a chlorine atom in a compound that has no chlorine? Supposedly, library spectra are the gold standard for identification work. Who looks at these library spectra when they are generated, when they are added to GNPS, when they are transferred into MassBank of North America, and when they are imported into Pubchem Compound? Anyone curious?

Compound Metadata

Name	Value
total exact mass	350.1552
SMILES	C#CCOS(=O)OC1CCCCC1OC2=CC=C(C=C2
SMILES	CC(C)(C)C1=CC=C(C=C1)OC2CCCCC2OS(=
pubmed id	n/a
molecular formula	C19H26O4S
InChIKey	ZYHMJXZULPZUED-UHFFFAOYSA-N
InChI	InChI=1S/C19H26O4S/c1-5-14-21-24(20)23- H,6-9,14H2,2-4H3
cas number	2312-35-8

Mass Spectral Metadata

Name	Value
author	mwang87, Dorrestein/Touboul, lfnothias
charge state	1.0000
exact mass	364.1380
instrument	Q-Exactive Plus Orbitrap Res 70k

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