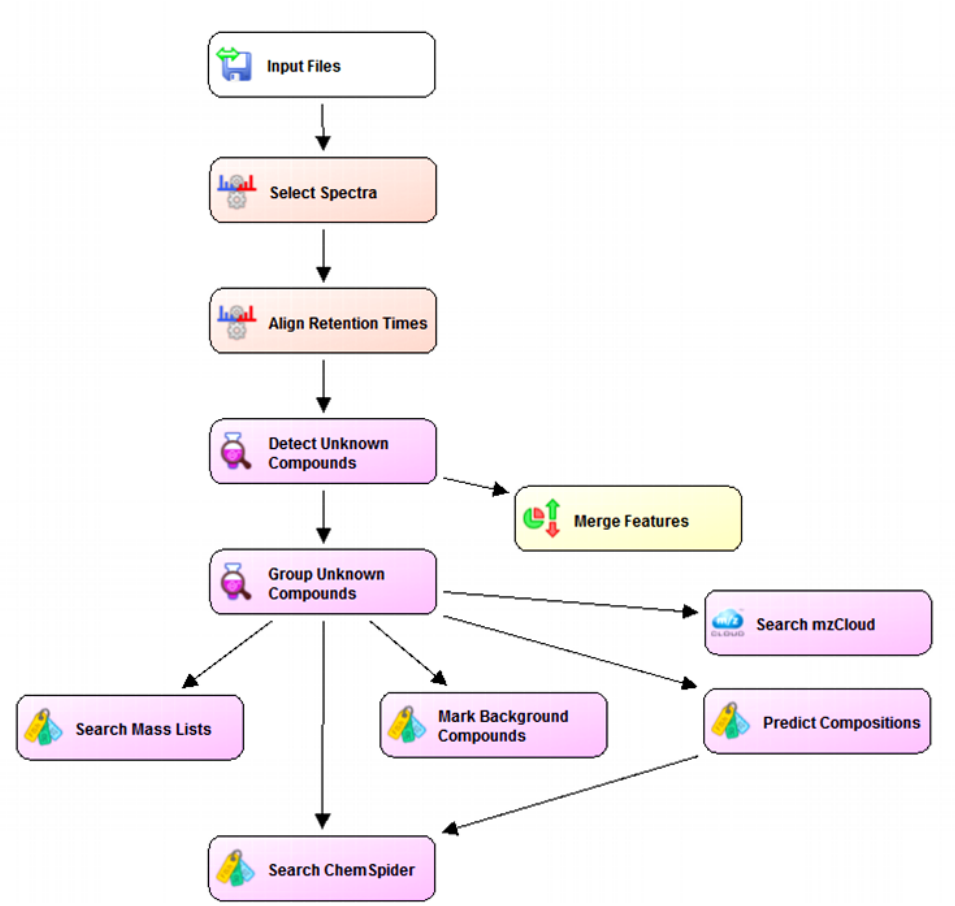

Figure S1. An example of Compound Discoverer workflow for analysis and annotation of PCI and NCI spectral data.

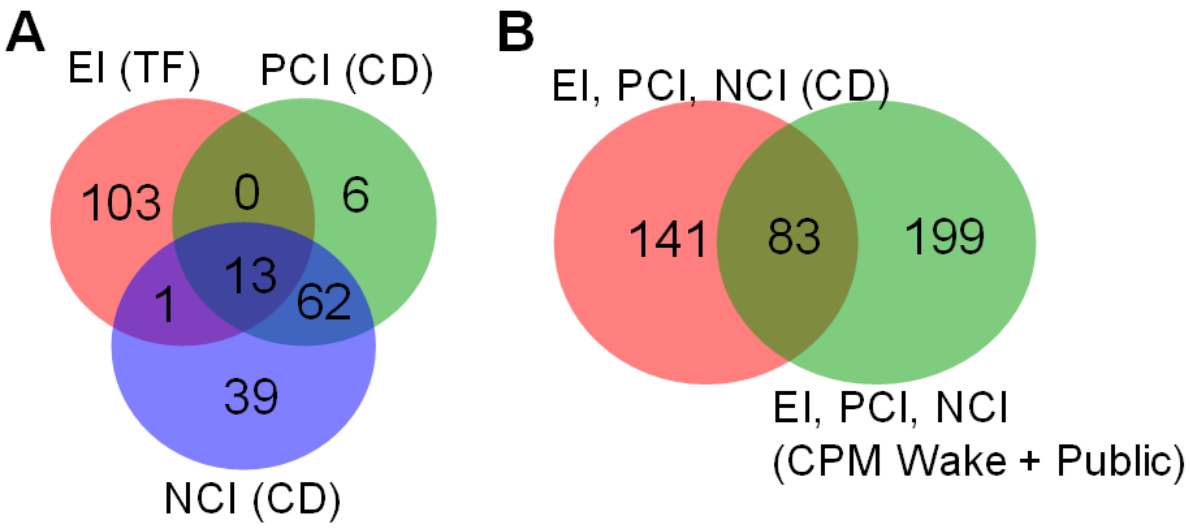

Figure S2. (A) Comparison of metabolite coverage for EI-MS, PCI-MS, and NCI-MS annotations obtained using commercial workflows from TraceFinder 4.1 and Compound Discoverer 2.1. (B) Comparison of combined metabolite coverage for EI-MS, PCI-MS, and NCI-MS annotations obtained using commercial workflows from TraceFinder 4.1 and Compound Discoverer 2.1 when compared against open source tools (MS-DIAL 3.9, MS-FINDER 3.22) in addition to the Wake Forest CPM spectral and retention time library.

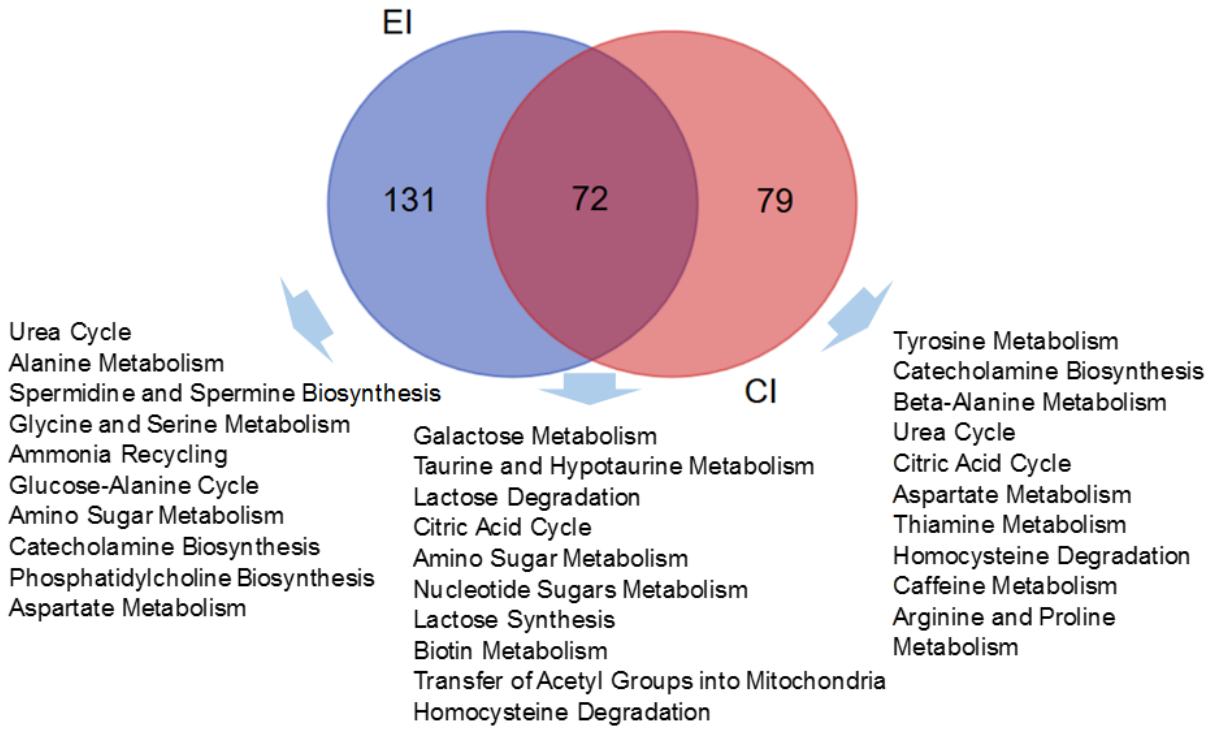

Figure S3. Pathway analysis for overlapping and unique metabolites for EI-MS and CI-MS quantified metabolites.

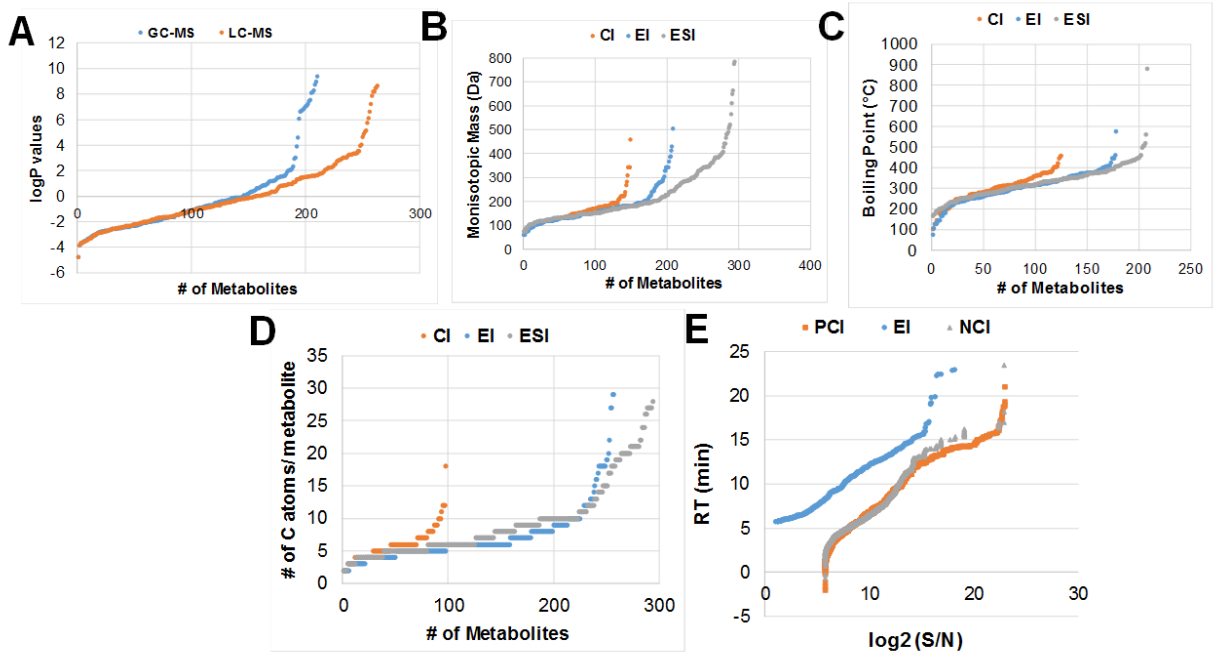

Figure S4. Molecular properties of the metabolites covered across the ionization methods and platforms (A) logP (measure of compound polarity) for the two compared platforms, GC-MS, and LC-MS, (B) Monoisotopic mass distribution of the compounds amenable to CI, EI and ESI modes of analysis, (C) Boiling point distribution of the compounds amenable to CI, EI and ESI modes of analysis; (D) No. of Carbon atoms/ metabolites distribution of the compounds amenable to CI, EI and ESI modes of analysis. (E) Shows the correspondence of RT (min) against log2 (S/N) for the three modes of analysis for the unique and shared metabolites.

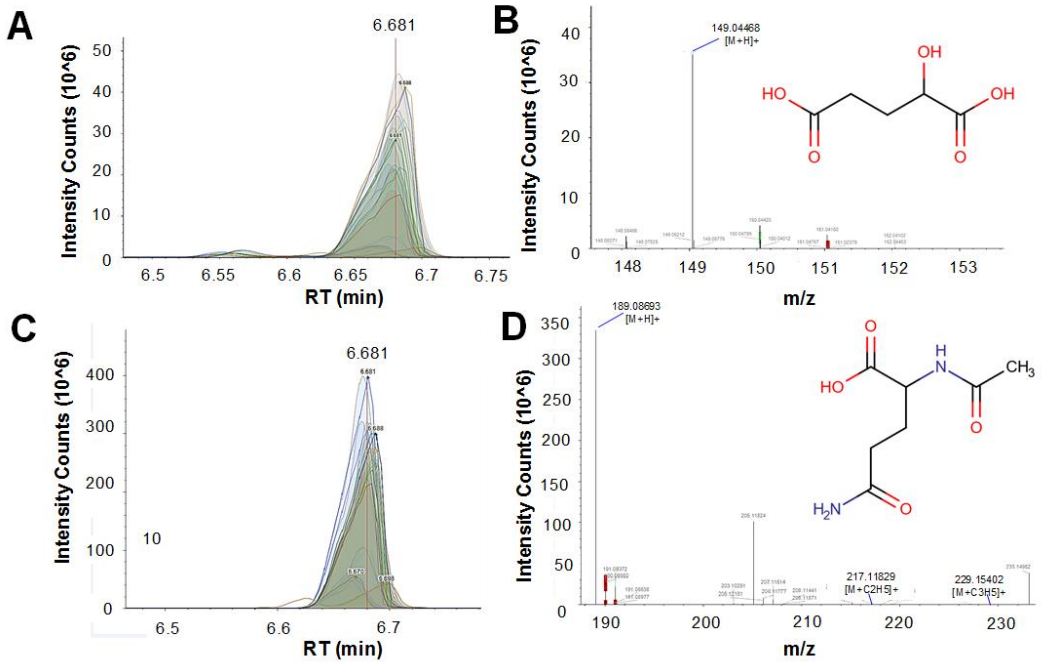

Figure S5. GC-PCI-MS interpretation using Compound Discoverer. (A) EIC for 2-hydroxyglutarate ($C_5H_8O_5$; monoisotopic mass: 148.03717), (B) MS1 spectrum for 2-hydroxyglutarate; (C) EIC for N-acetyl-L-glutamine ($C_7H_{12}N_2O_4$; monoisotopic mass: 188.0797), (D) MS1 spectrum for N-acetyl-L-glutamine.