



PRIORITIZING AND IDENTIFYING POLAR EMERGING CONTAMINANTS IN WASTEWATER BY HILIC-HRMS

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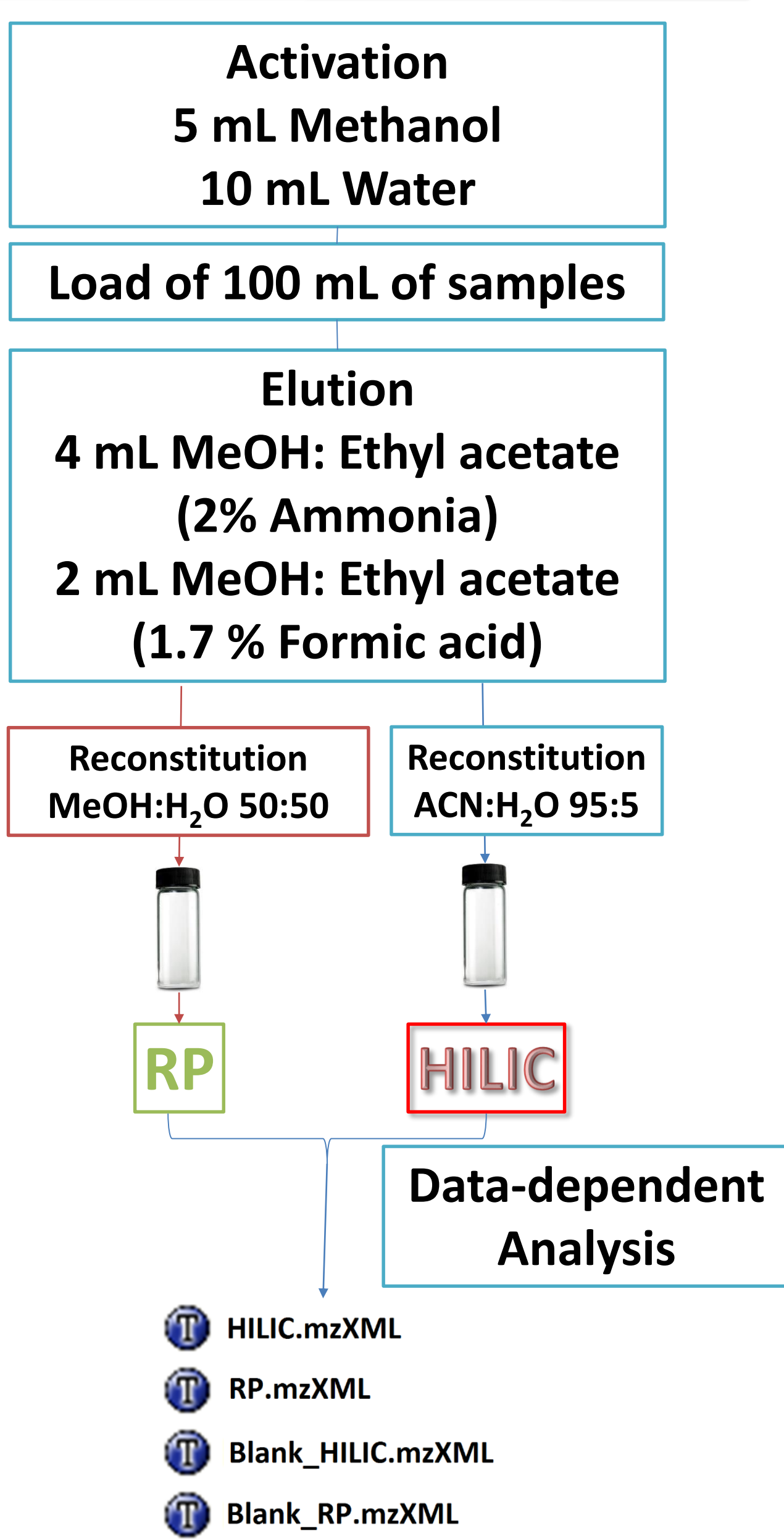
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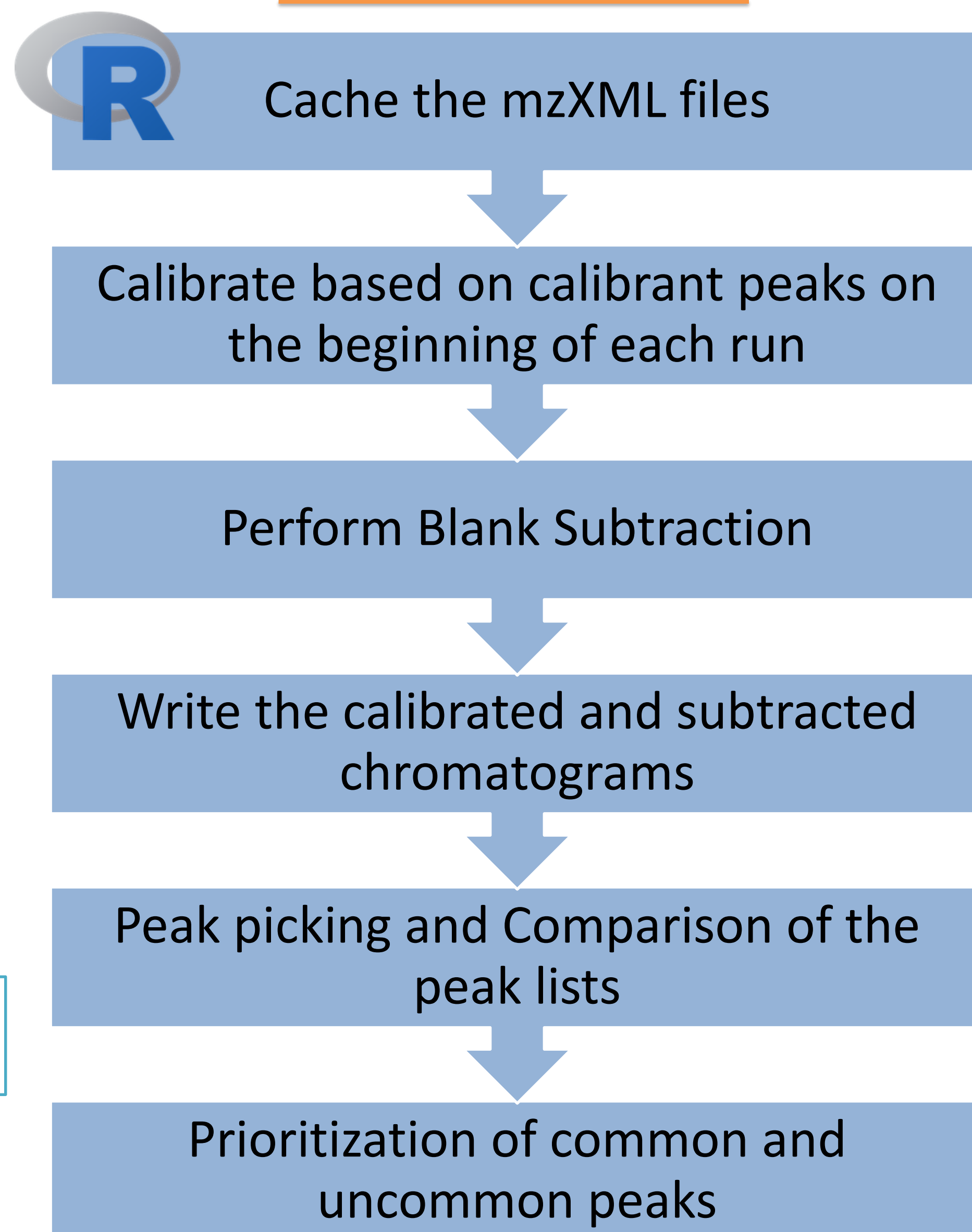
Abstract

Hydrophilic Interaction Liquid Chromatography (HILIC) is a separation technique used for the determination of polar compounds. A target HILIC-QTOFMS screening method was developed and validated for a fraction of representative emerging contaminants (>900 compounds) and its complementarity to reversed phase (RPLC) was proven by detecting additional to RPLC compounds in wastewater samples. In order to prove the usefulness of HILIC-QTOFMS analysis in non-target screening, an in-house computational workflow was also developed. Influent wastewater samples, along with procedural blanks, were prepared and injected in both HILIC-QTOFMS and RPLC-QTOFMS using data-dependent acquisition mode. Raw data was converted to mzXML, loaded in the R-workspace and recalibrated based on the calibrant peaks in the beginning of each chromatogram. Then, subtraction of procedural blank from samples was performed and the chromatograms were exported again as mzXML files. Peak picking was implemented on the subtracted files based on centWave algorithm included in the XCMS package. HILIC and RPLC peak lists were compared and results showed that HILIC is important as a complementary technique, especially for the identification of polar unknown compounds. It was revealed that many common peaks can be detected in HILIC at higher intensity than in RPLC, especially those well-retained in HILIC. Moreover, approximately 20% of HILIC peaks remained undetected in RPLC. Common peaks were prioritized after setting intensity and retention time restrictions, while unique peaks in HILIC were prioritized by intensity. Retention time restrictions were related to the fact that polar compounds should be retained in HILIC, while it is expected to elute in the void volume of the RPLC gradient. Investigation of common and unique peaks in HILIC led to the successful identification of many polar compounds (88 compounds at level 3 and above mainly belonging to the class of surfactants).

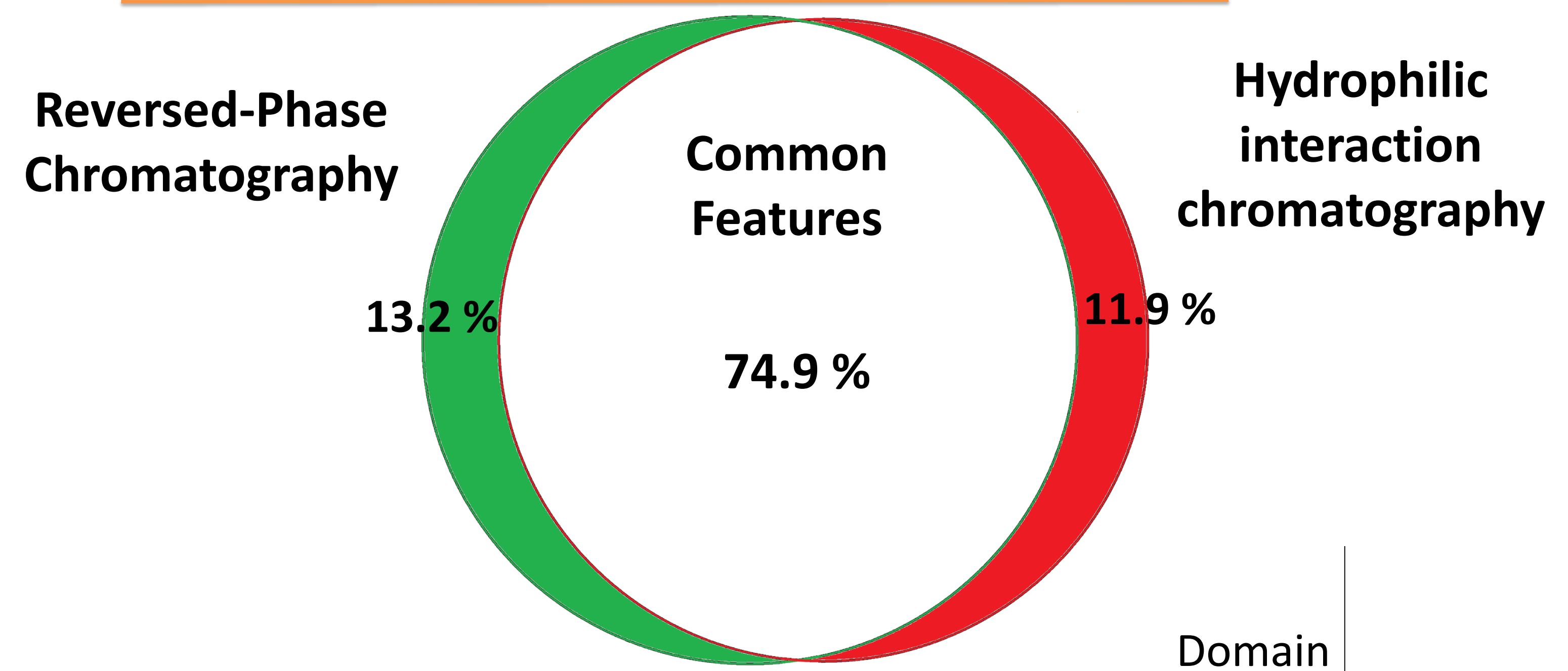
Analytical Protocol



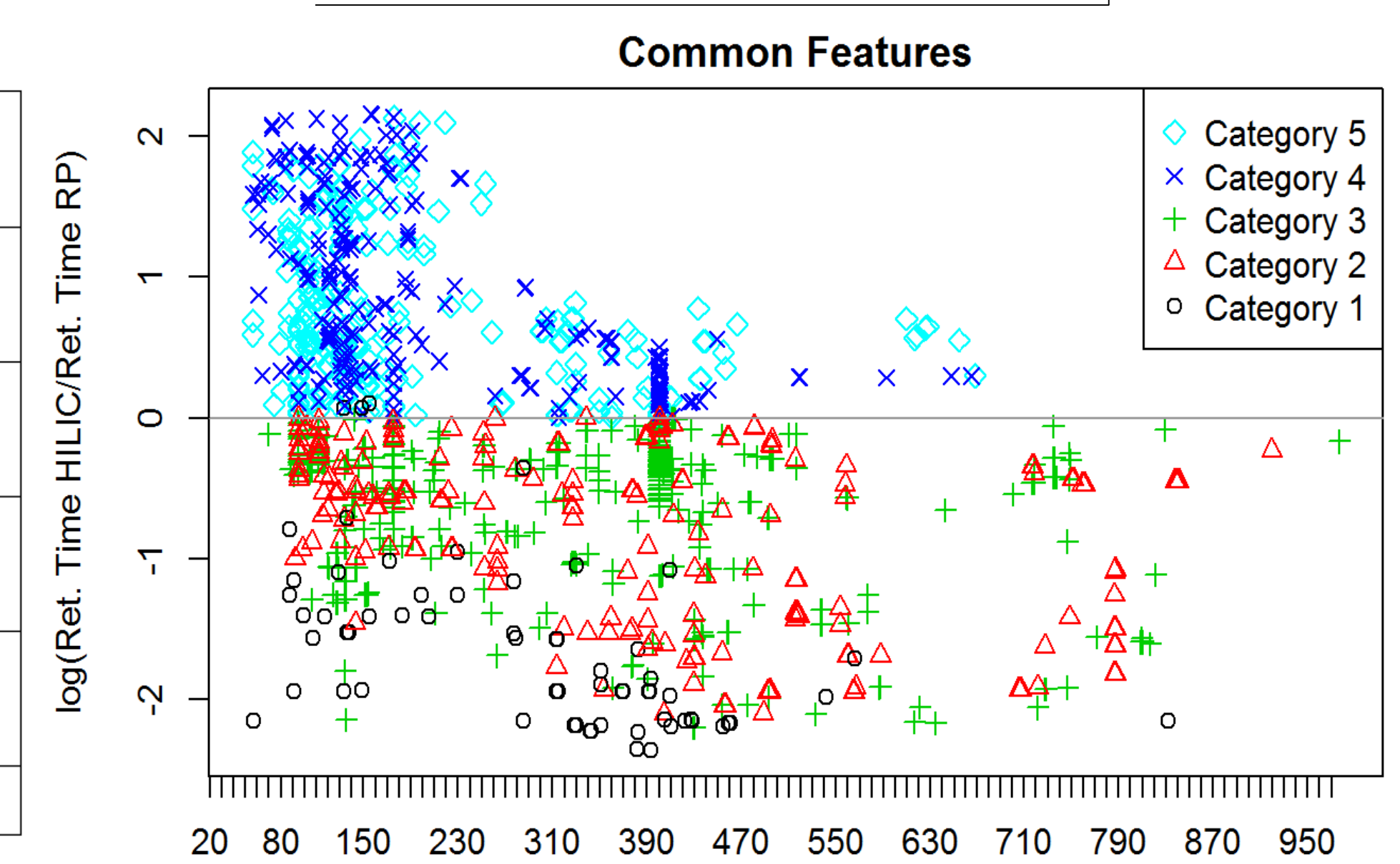
Programming



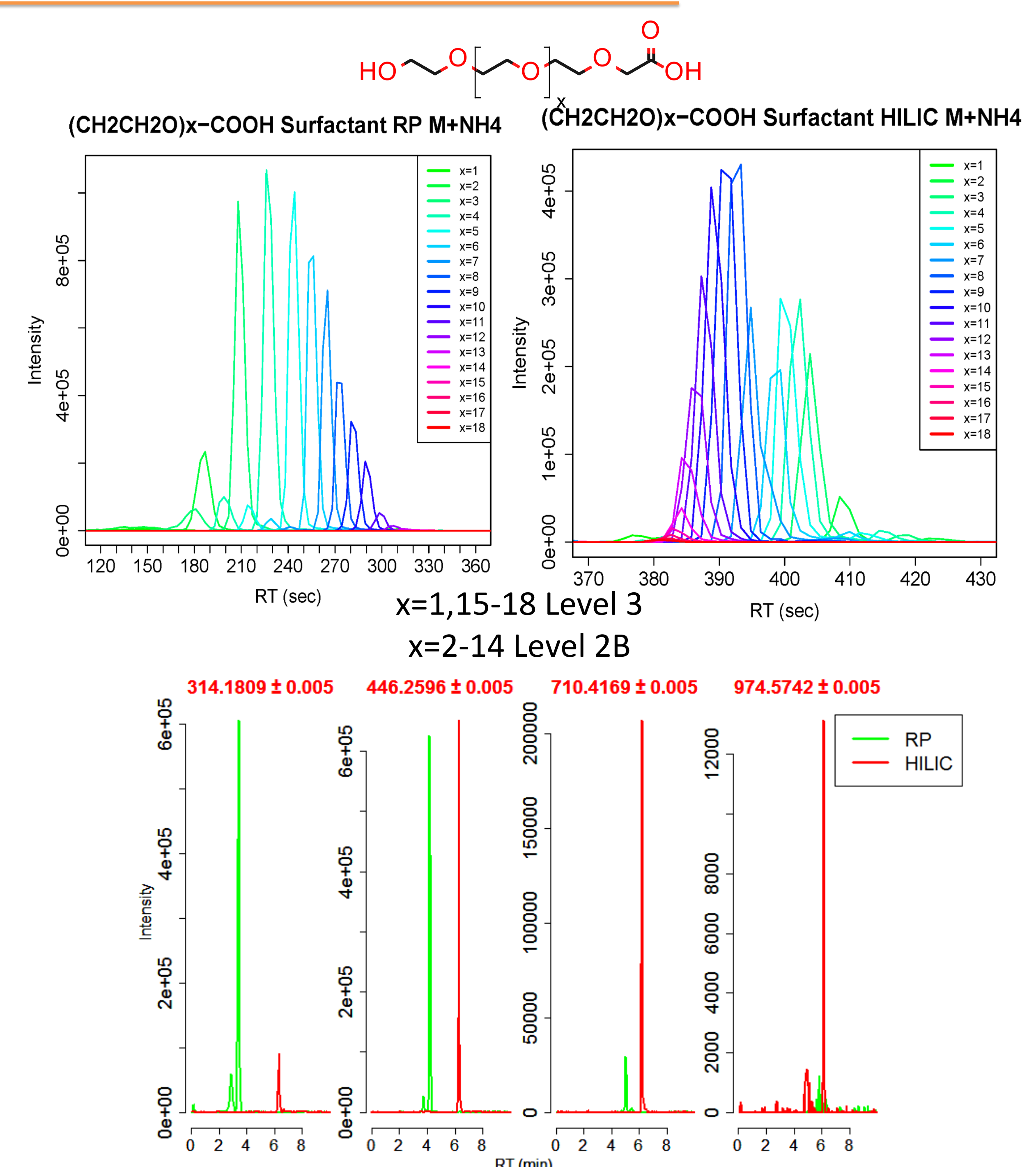
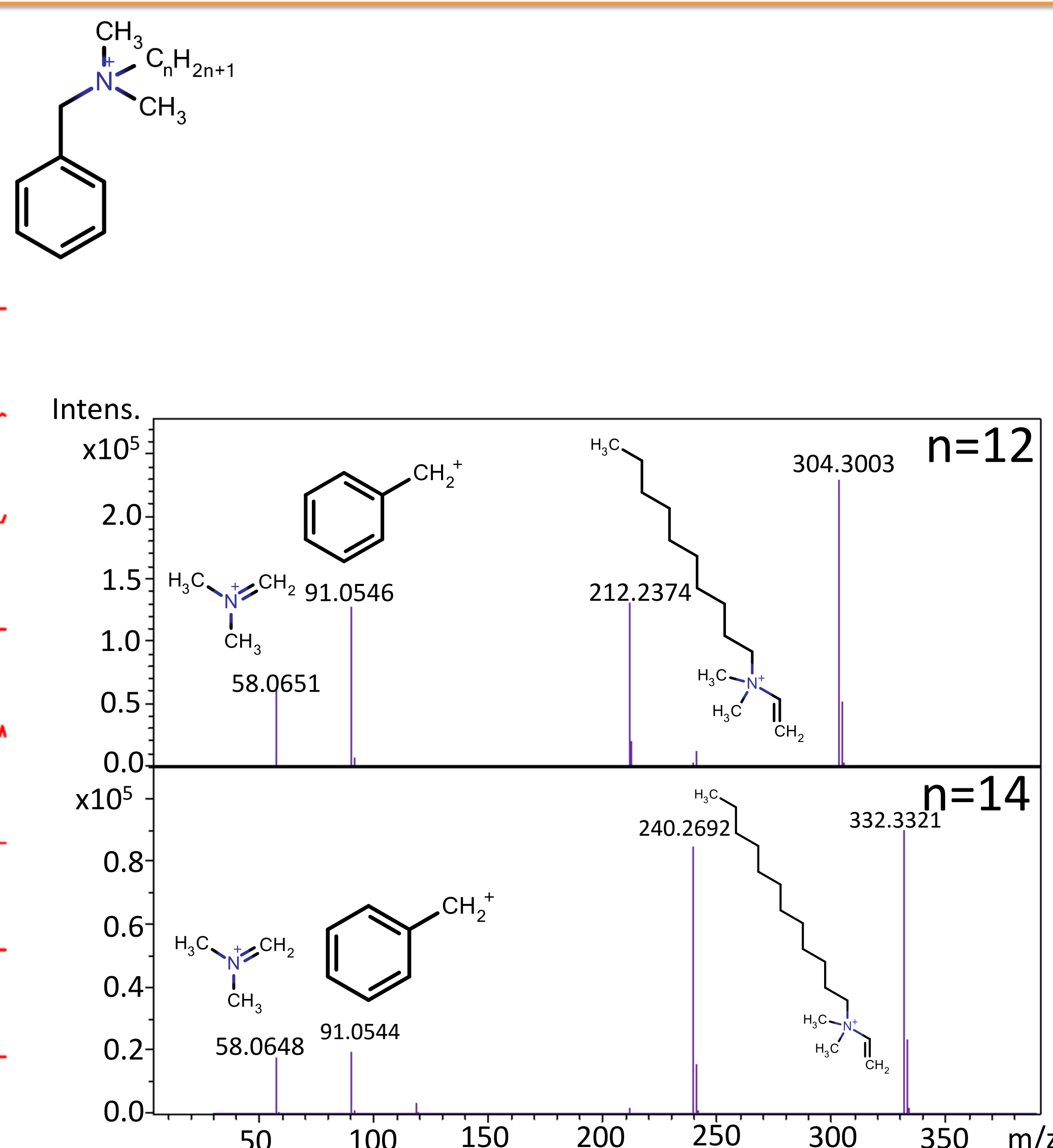
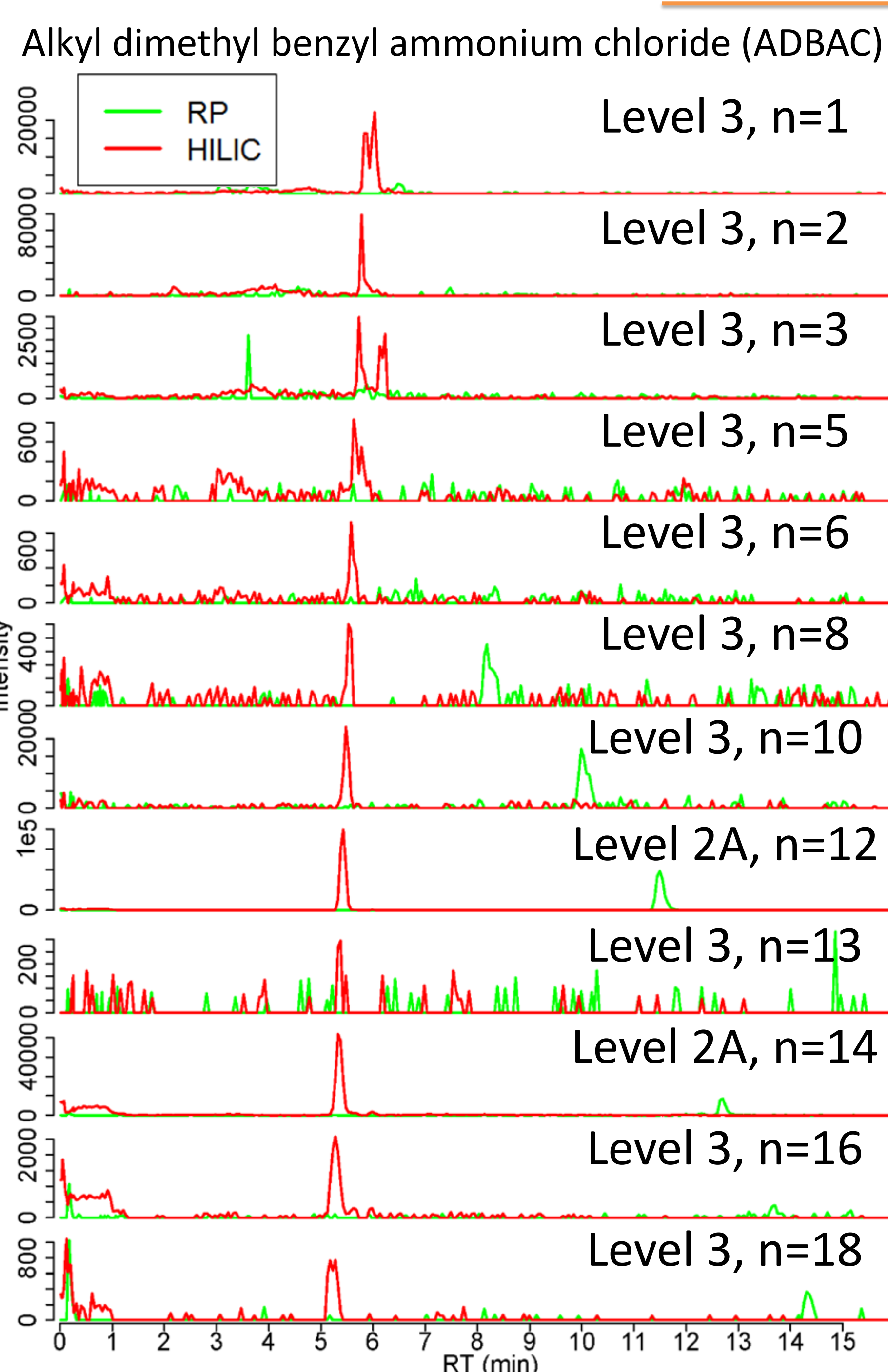
Prioritization of common peaks



Category	Retained in HILIC (k'>1)	Retained better in HILIC than in RP	Better response in HILIC
5	✓	✓	✓
4	✓	✓	✗
3	✓	✗	✓
2	✓	✗	✗
1	All the rest cases		



Non-target Identification of series of homologues contaminants



Intensity is increasing as polarity is increasing in HILIC. Last members of this homologue series are only detectable in HILIC



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