Method Development for Amine Analysis Using Ion-Pair based High Performance Liquid Chromatography (IP-HPLC)

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Importance of Accurate Amine Analysis

- Confirm amine quality
- Confirm amine blend formulation
- Check for amine carry-over in off-gas
- Provide early detection of process anomalies

Common Chromatographic based techniques used for amine capture solvents

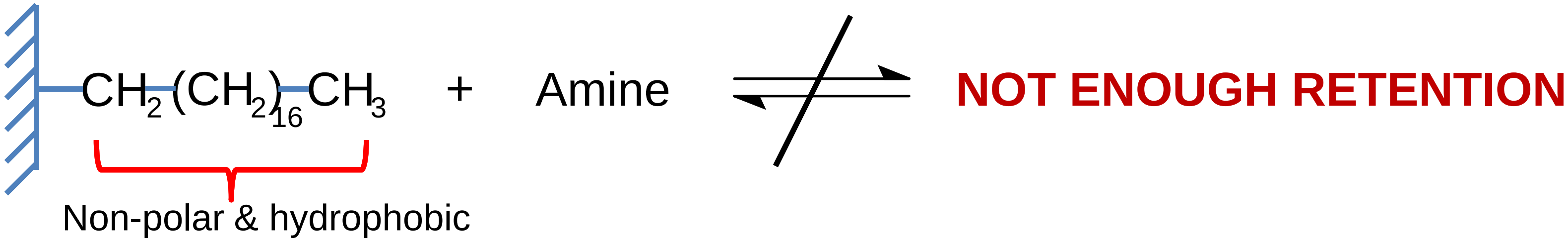
Technique	Concerns
Gas Chromatography (GC)	Peak tailing for highly polar amines, not preferred for solid amine
Ion-Exchange Based Liquid Chromatography (IE-LC)	Strong salt and acid based mobile phases limits the use with MS
Reversed Phase Liquid Chromatography (RP-LC)	Not polar enough to retain amines
Ion-Pair based Liquid Chromatography (IP-LC)	Rare for amines in CO_2 capture application but promising

Ion-Pair Based Liquid Chromatography (IP-LC)

- Higher affinity to polar amines leading to a successful separation (compared to RP-LC)
- Selectivity fine-tunable via ion-pair types compared to IC-LC
- Peak tailing more manageable compared to GC-MS
- Can be modified for analysis of amines and anionic species in one single column

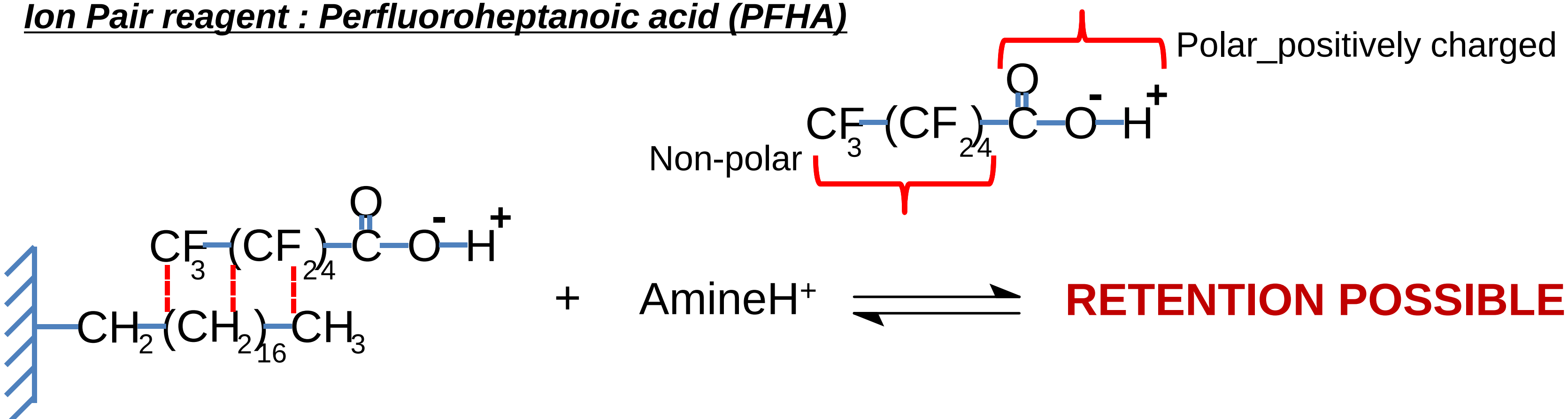
HPLC_ION PAIR TECHNIQUE FOR AMINE SEPARATION

- **Non-polar column with the internal surface containing long chain hydrocarbon (e.g. C8 and C18), normally will not effectively retain amines especially high polar amines.**

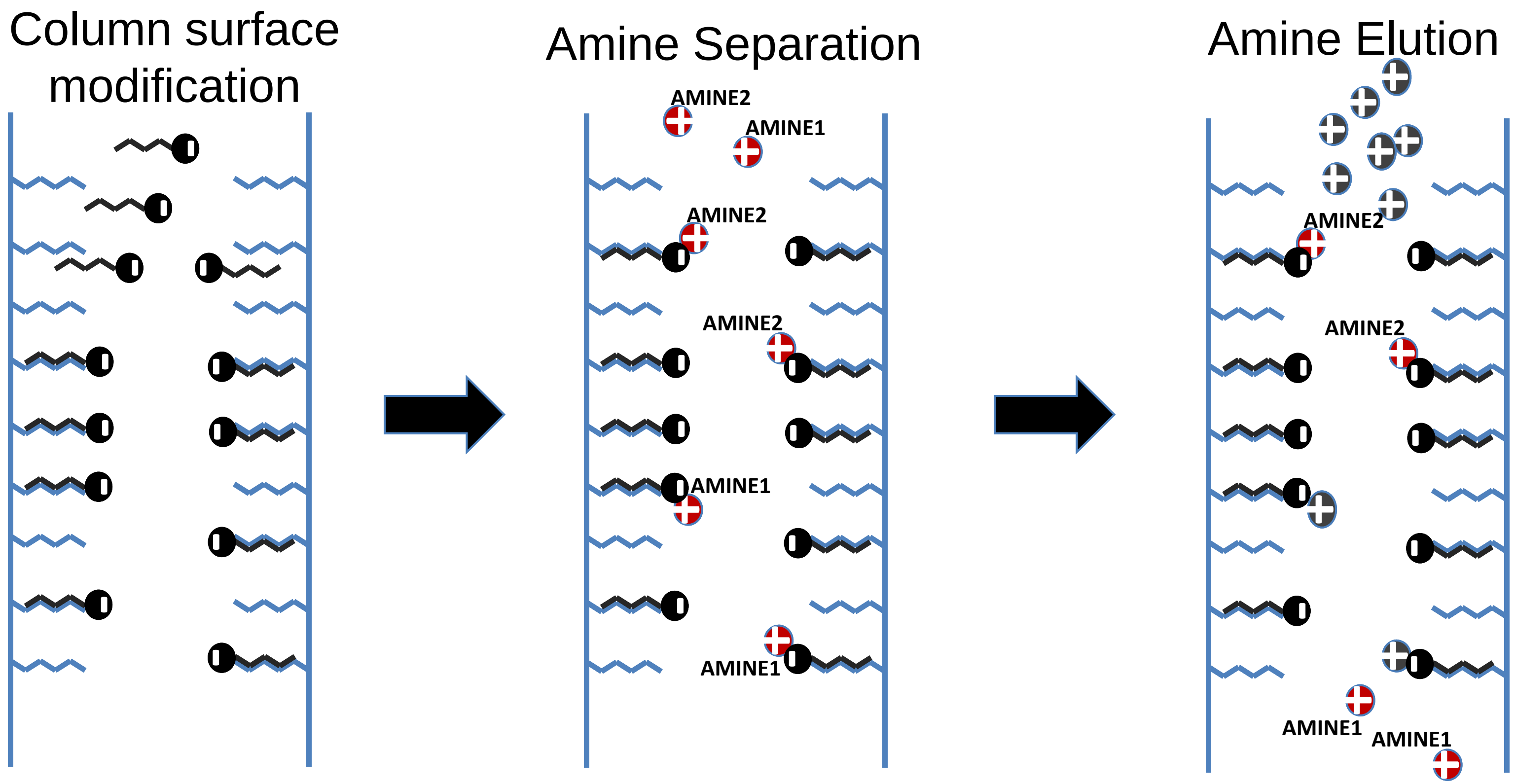


- **Ion-pair reagent with one side of the molecule being non-polar long chain hydrocarbon (e.g. C4 – C8) and the other side containing positively charged group can be used to modify the column internal surface more suitable for amine separation**

<u>Ion Pair reagent : Perfluoroheptanoic acid (PFHA)</u>



Ion Pair Mechanism for Amine Separation

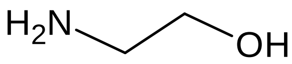


Research Objectives

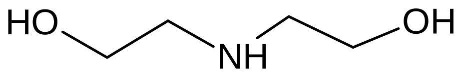
- To develop the IP-HPLC method capable of analysis of different types of amines commonly used in the CO_2 capture process (e.g. single and bi and tri blends)
    - Optimization of isocratic run condition
    - Optimaztion of pH step gradient condition
- To explore different mobile phase combinations to separate amines.

Target Amines

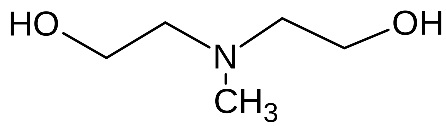
Conventional Amines (1°, 2°, 3°)



MEA

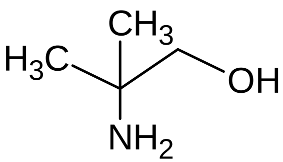


DEA



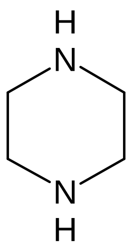
MDEA

Hindered Amines

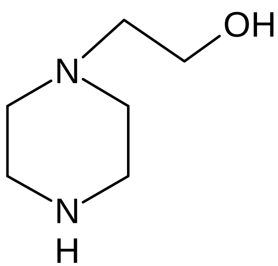


AMP

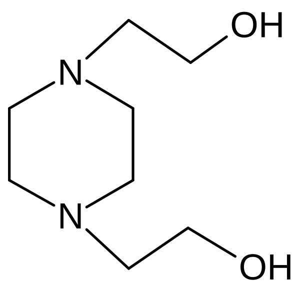
Cyclic Amines



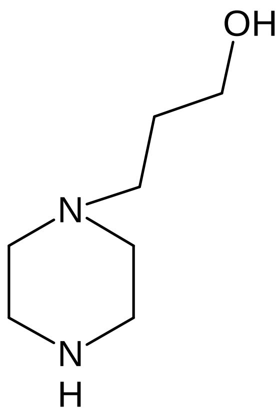
PZ



HEP



DIHEP



1-PZpropanol

Ion pair test conditions

Hypersil Gold aq Column

- Highly pure encapped silica
- Functionalized with carbon 18 for compound separation

Selected Ion pair reagents for test

- Perfluorobutanoic acid (PFBA, with C4)
- Pefluoroheptanoic acid (PFHA, with C7)
- Perfluorooctanoic acid (PFOA, with C8)

} Strong ion pair reagents

- Pentanoic acid (C5 without fluorine)

} Weak ion pair reagent

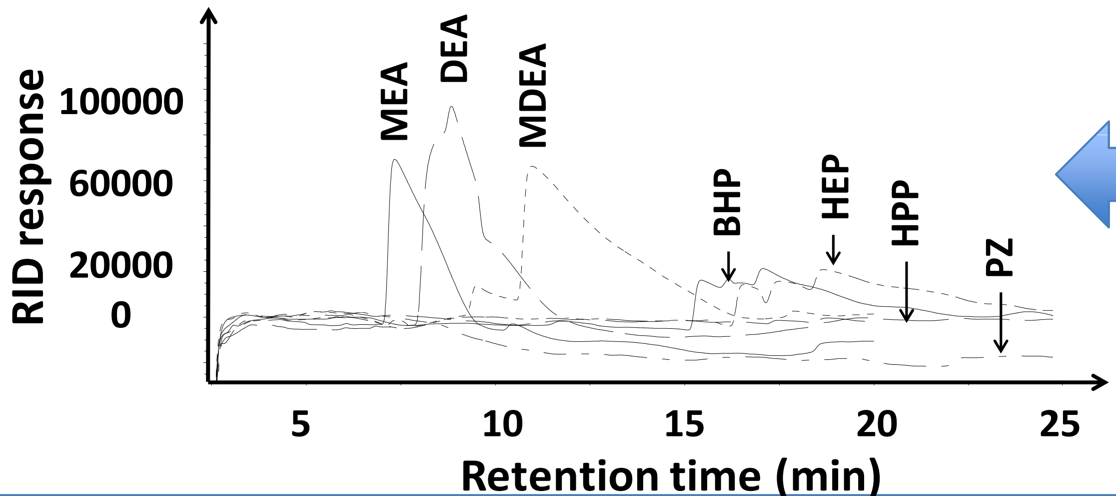
Mobile phases

- Formic acid
- Ammonium formate, Acetate (salt)
- Triethylamine (TEA), NH_3 in methanol, and NH_4OH (pH)

Results and Discussion

Optimizing Isocratic Mobile Phase Condition

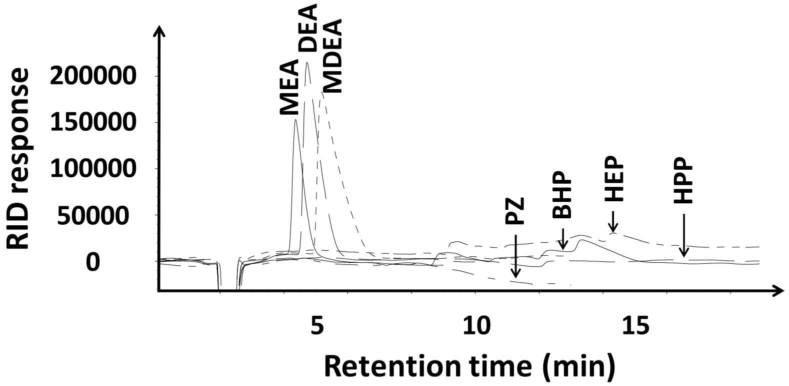
- Establish a baseline aqueous mobile phase mixed with an organic modifier
- Several screening tests were done using PFBA, PFHA, and PFOA
  - PFBA: Did not exhibit sufficient retention of all the amines
  - PFOA: Unsuitable due to surfactant effect making mobile phase foamy
  - **PFHA: Able to retain most amines at minimum concentration, thus selected for further development**



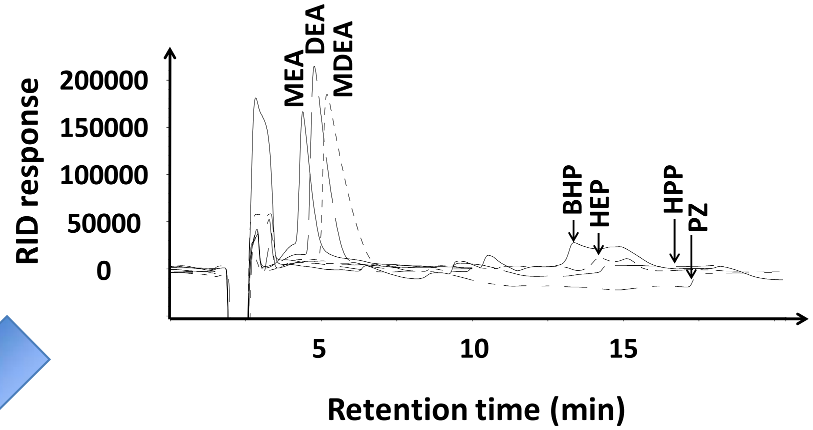
Mobile Phase
10 mM PFHA aqueous containing;
(a) 1% formic acid @ pH 3

Effect of Mobile phase Ingredients (e.g. pH)

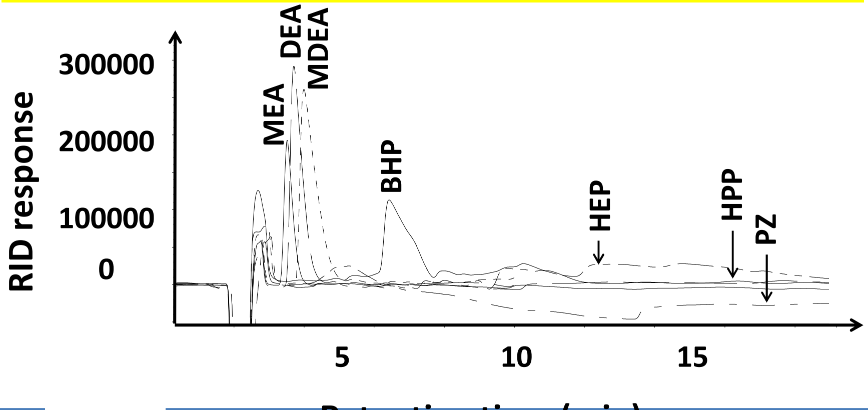
10mM PFHA + 0.5% formic acid and 0.15 M ammonium formate/ACN @ 95:5 volume ration @ pH 3.8



10 mM PFHA + 0.15 M ammonium formate/ACN @ volume ration 95:5 @ pH 4.7

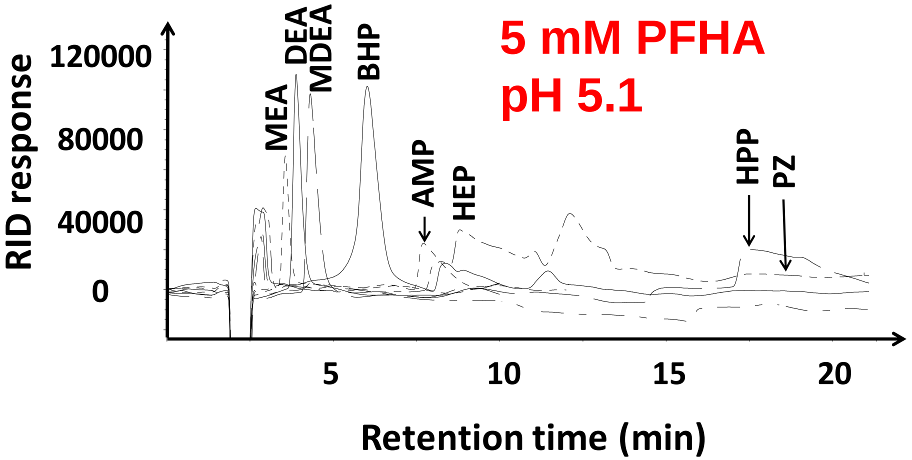


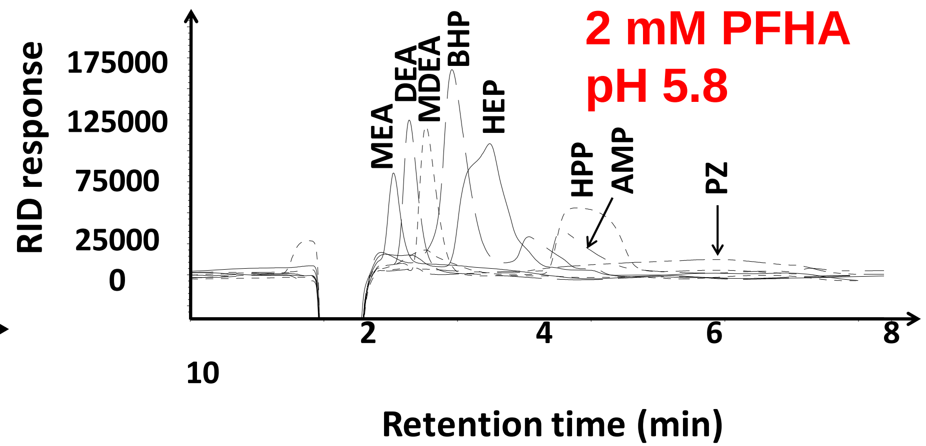
10 mM PFHA + 0.3 M ammonium formate/**ACN** @ **95:5 volume ratio @ pH 4.8**

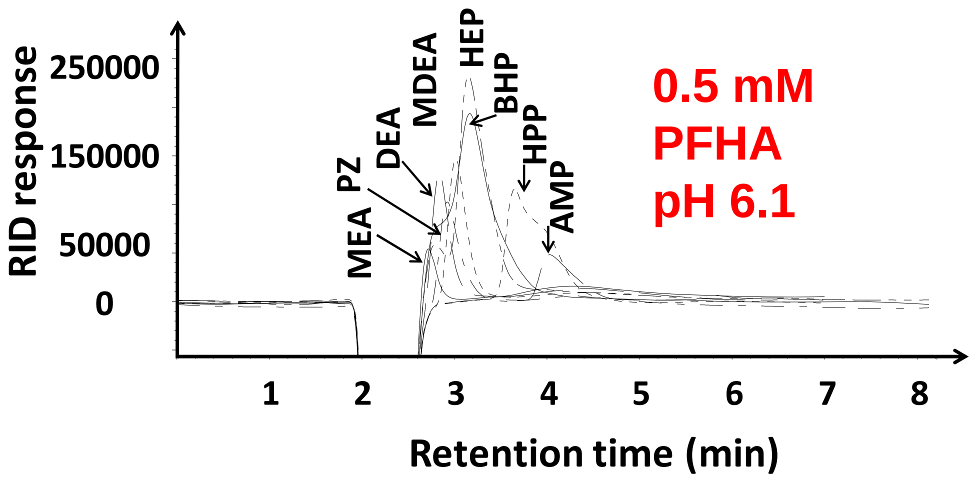


- **pH is key in amine separation**
  - Cyclic amines require higher pH for a complete separation

Effect of PFHA Concentration

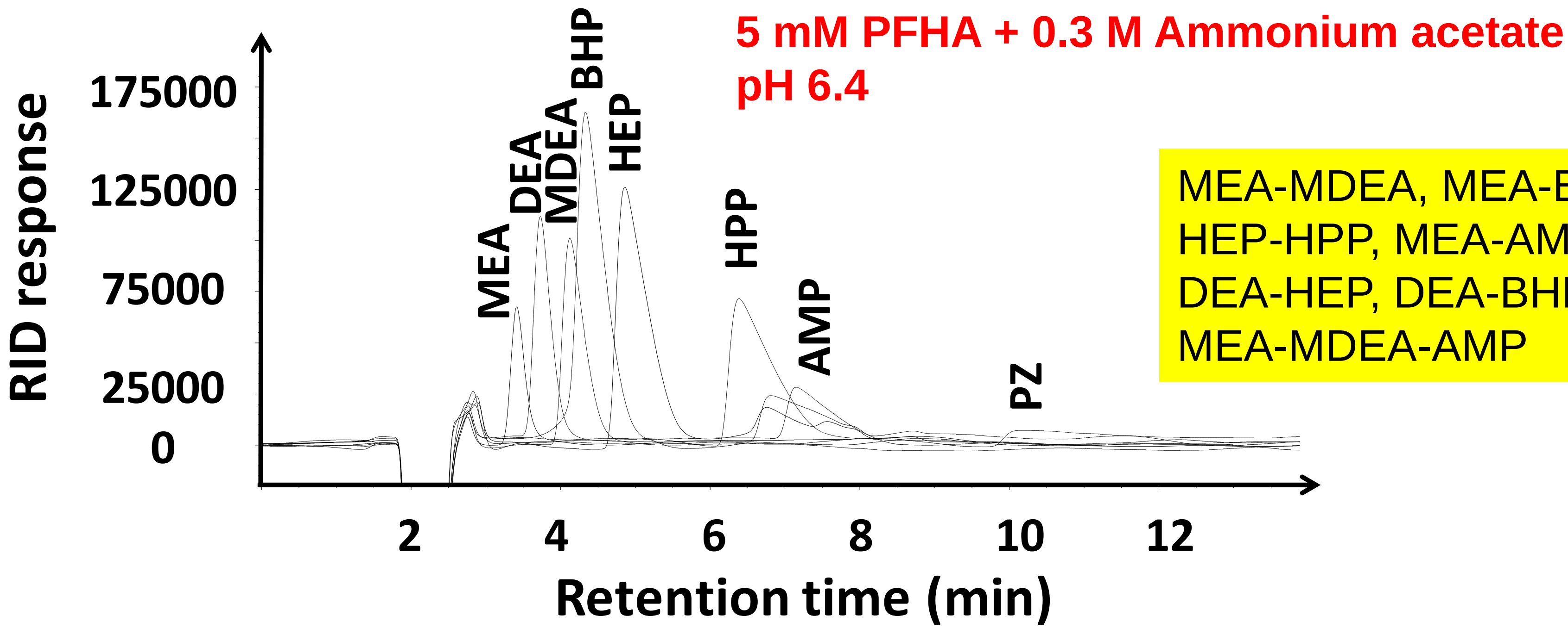






- 5 mM was the optimized PFHA concentration

Effect of Fine-Tuning pH in Improving Separation and Elution of Heterocyclic Amines



MEA-MDEA, MEA-BHP, HEP-HPP, MEA-AMP, DEA-HEP, DEA-BHP
MEA-MDEA-AMP

To successfully retain, elute, and separation cyclic amines containing 2 amino groups;

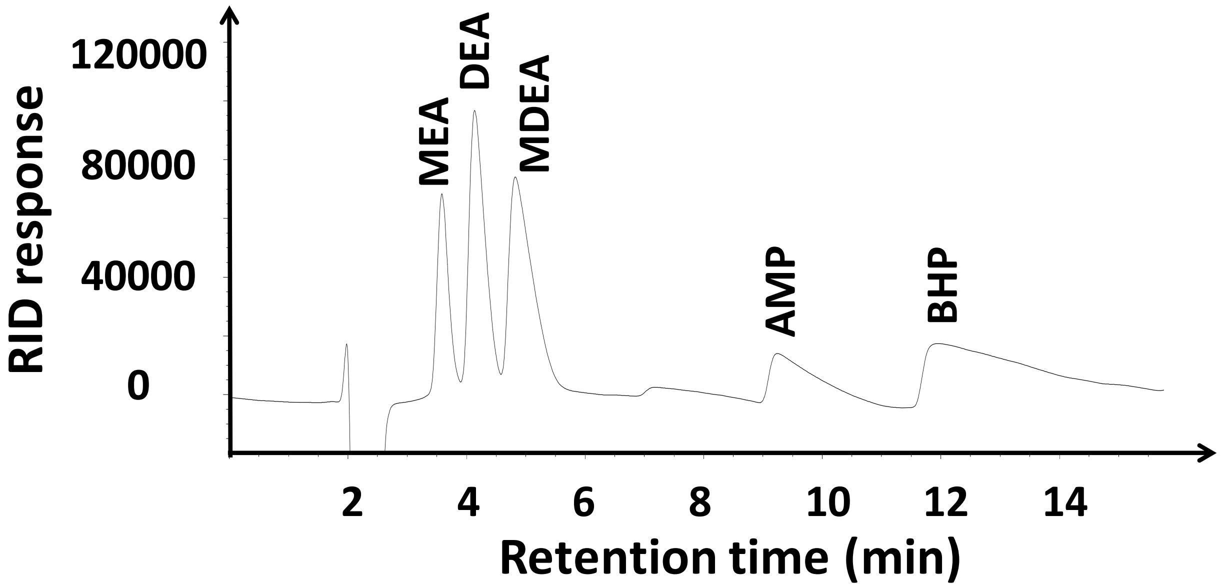
- **Mobile phase pH must be adjusted between 2 pKa of amines**

Formulation of pH Step Gradient Mobile Phase Conditions

- To further improve the use of this technique so as to allow all amines in any mixtures to be analyzed

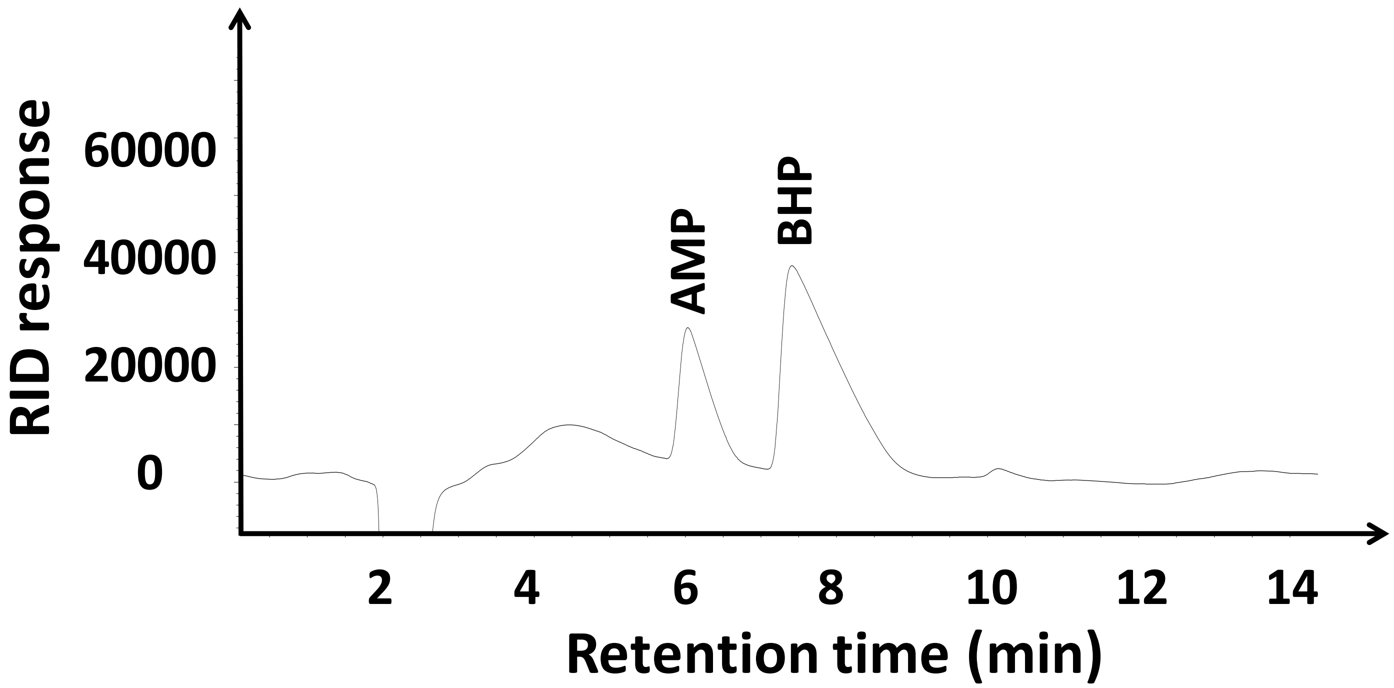
pH Gradient Step 1: MEA, DEA, MDEA

Run condition: 5 mM PFHA and 0.3 M ammonium acetate @ pH 4.5/1%ACN



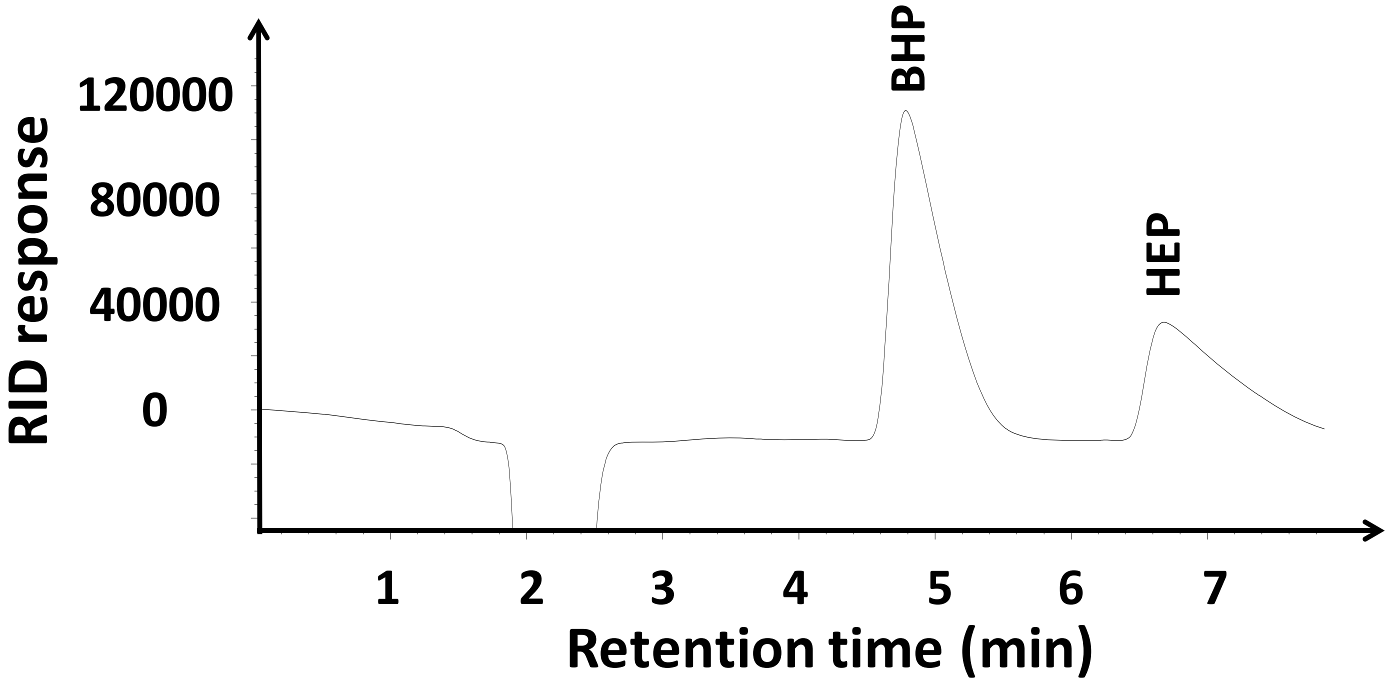
pH Gradient Step 2: AMP

Run condition: 5 mM PFHA and 0.3 M ammonium acetate @ pH 4.5/5% ACN



pH Gradient Step 3: BHP

Run condition: 5 mM PFHA and 0.3 M ammonium acetate @ pH 5.5 /5% ACN

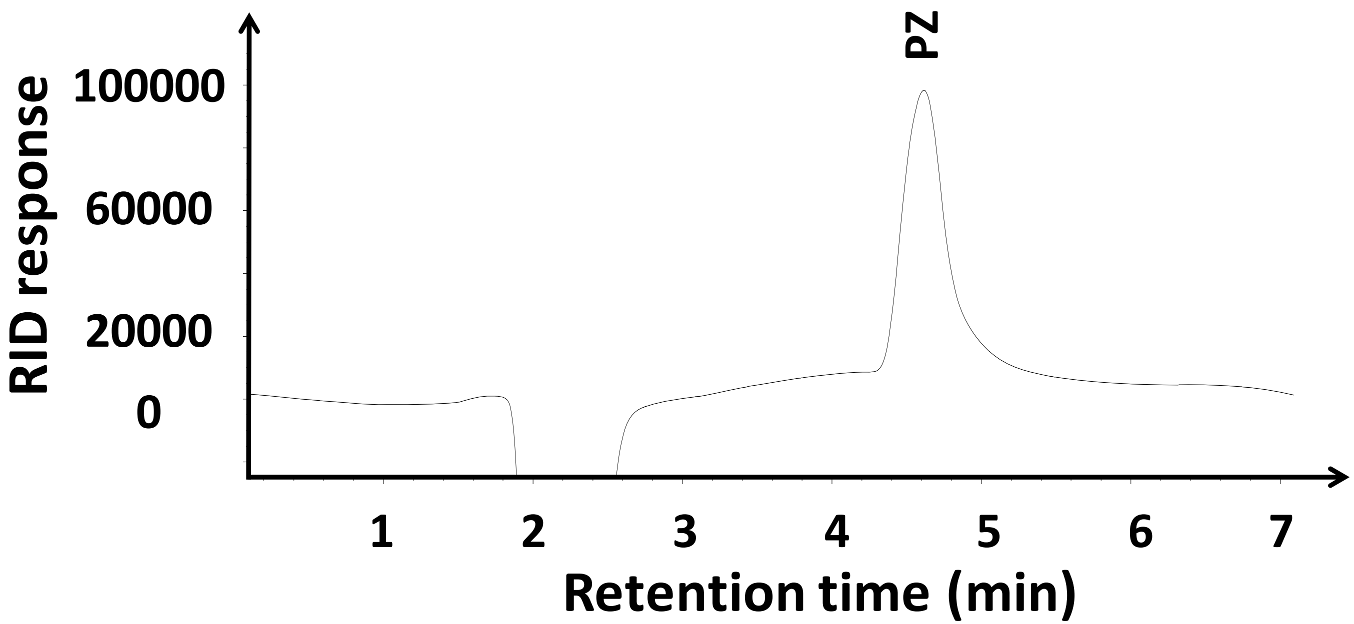


pH Gradient Step 4: HEP and HPP

Run condition: The opitimum isocratic run condition with 5 mM PFHA and 0.3 M ammonium acetate @ pH 6.4 /5% ACN

pH Gradient Step 4: PZ

Run condition: 5 mM PFHA and 0.3 M ammonium acetate @ pH 8 /5% ACN

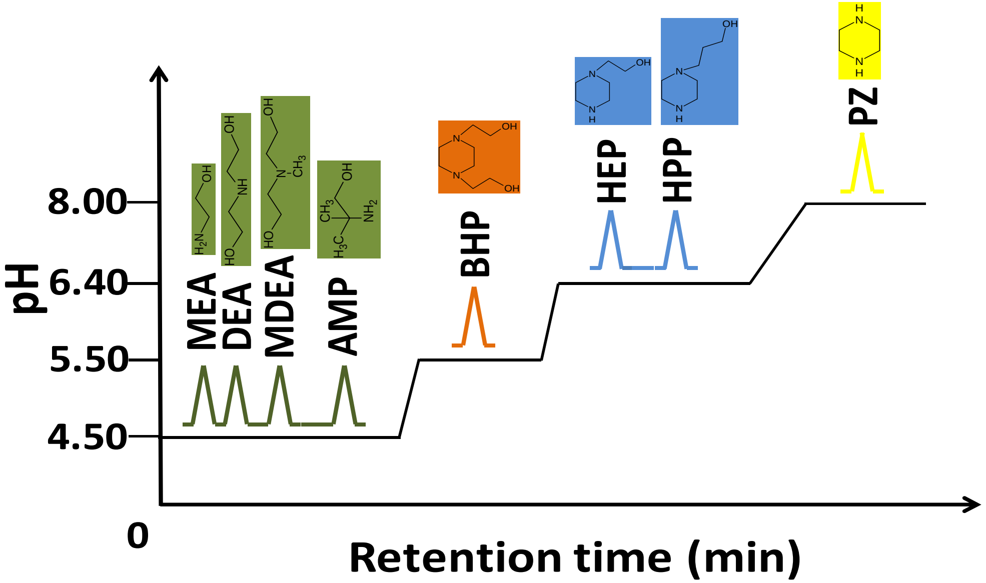


Summary of pH Step Gradient Run conditions

pH	Mobile Phase Volume (%) [1]A @ pH 4.5	[2]B @ pH 8	ACN	Amine Separated
4.5	99	0	1	MEA, DEA, MDEA
4.5	95	0	5	AMP
5.5	15	80	5	BHP
6.4	2	93	5	HEP and HPP
8.0	0	95	5	PZ

[1]5 mM PFHA and 0.3 M ammonium acetate adjusted to pH 4.5 by acetic acid
[2]5 mM PFHA and 0.3 M ammonium acetate adjusted to pH 8.0 by NH_4OH

pH Step Gradient Separation Chart



Conclusions

- Isocratic condition based ion-pair HPLC method has been developed which can analyze various industrial mixtures such as MEA-MDEA, MEA-BHP, HEP-HPP, MEA-AMP, or MEA-MDEA-HEP/HPP

- pH step gradient run conditions have also been developed capable of analysis of complex amine mixture containing any amines used this study; MEA, DEA, MDEA, AMP, BHP, HEP, HPP, and PZ

Acknowledgements

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