

SPE-164133

The Evaluation and Optimization of Hydrogen Sulfide Scavenger Applications Using Ion Mobility Spectrometry

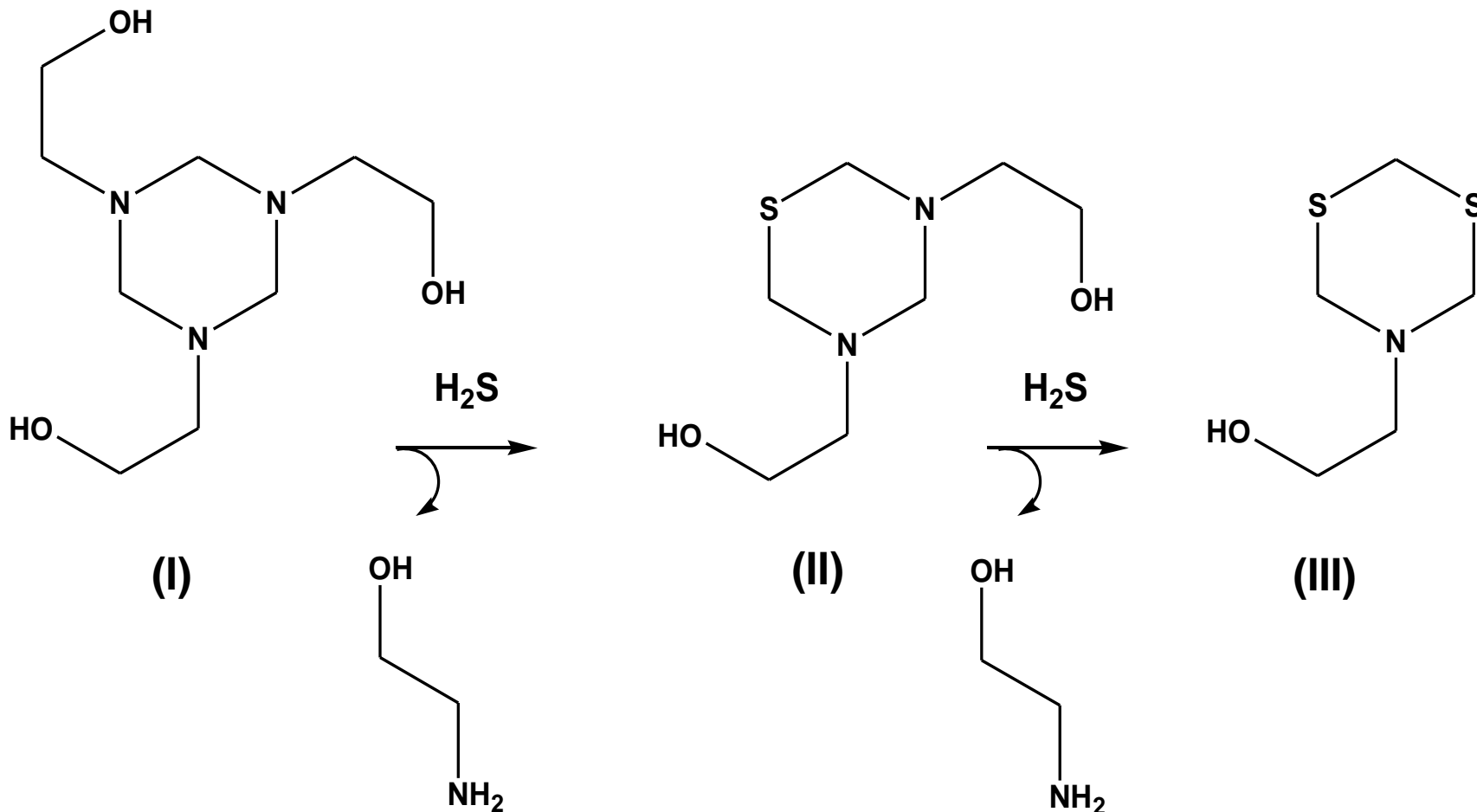
Ron Matherly (Baker Hughes) and Grahame Taylor (Baker Hughes)

Solid Deposition from Spent Triazine

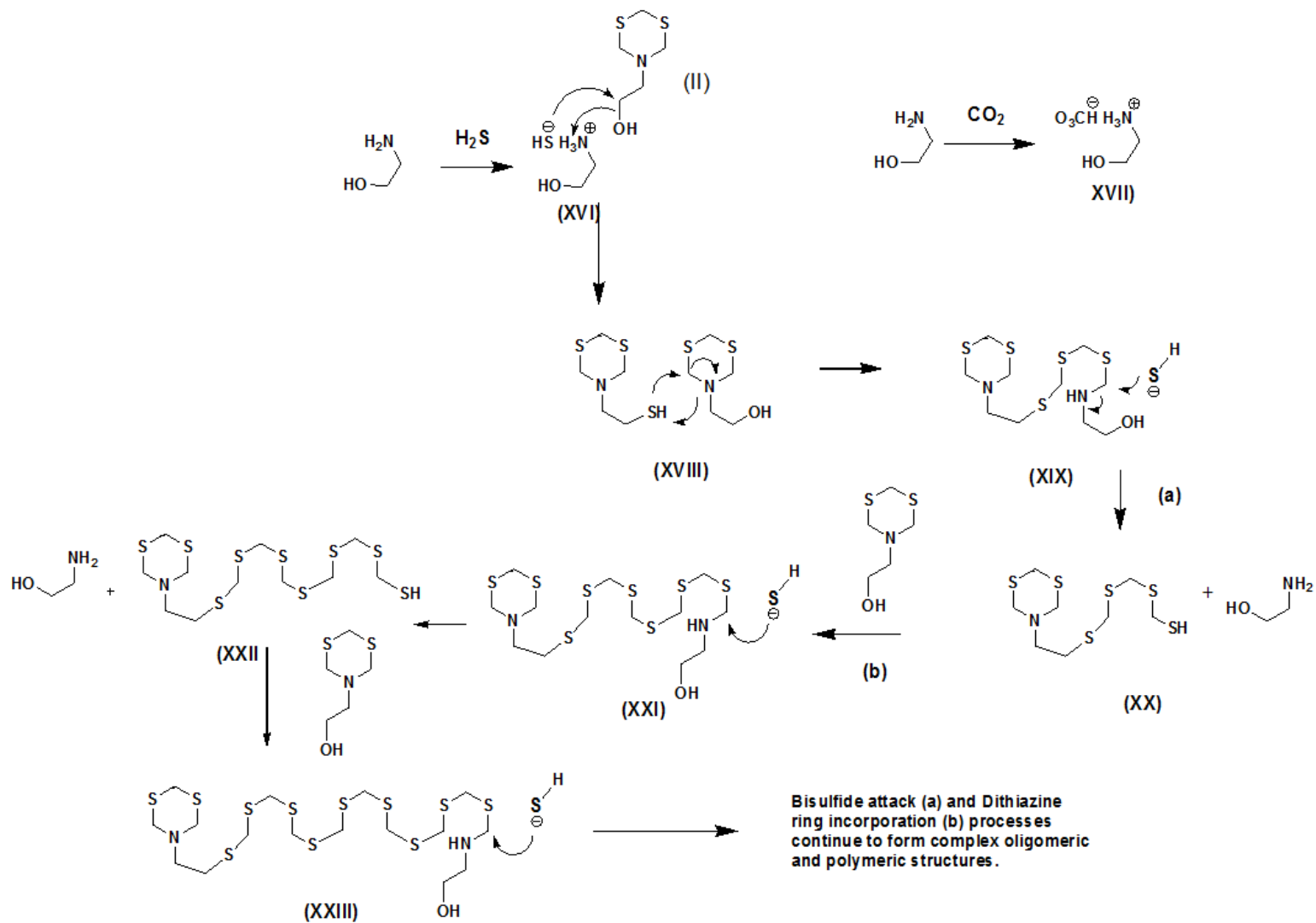
- 1,3,5-Tris(2-hydroxyethyl)-hexahydro-s-triazine (HHTT) is the most common triazine.
- After 60% spent – two phases occur followed by solids.
- Crystalline then amorphous solids are deposited
- Disposal of spent fluid containing solids problematic
- Amorphous solids very hard to inhibit, avoidance is the best policy.



1,3,5-Tris(2-hydroxyethyl)-hexahydro-s-triazine (HHTT) reaction scheme



Formation of amorphous dithiazine



Phase separation from heavily spent HHTT fluids



Technique Definition

F = Field

A = Asymmetric

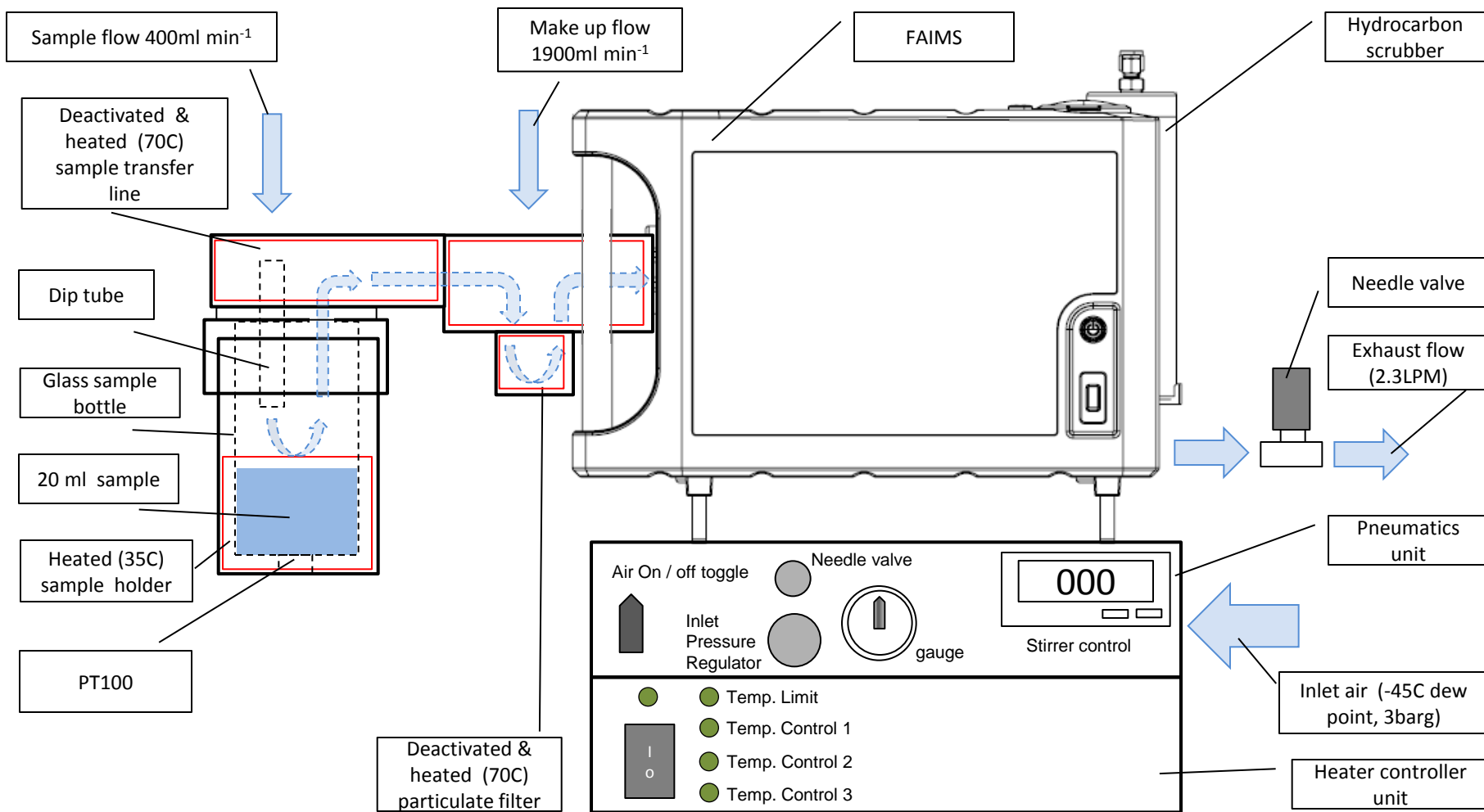
I = Ion

M = Mobility

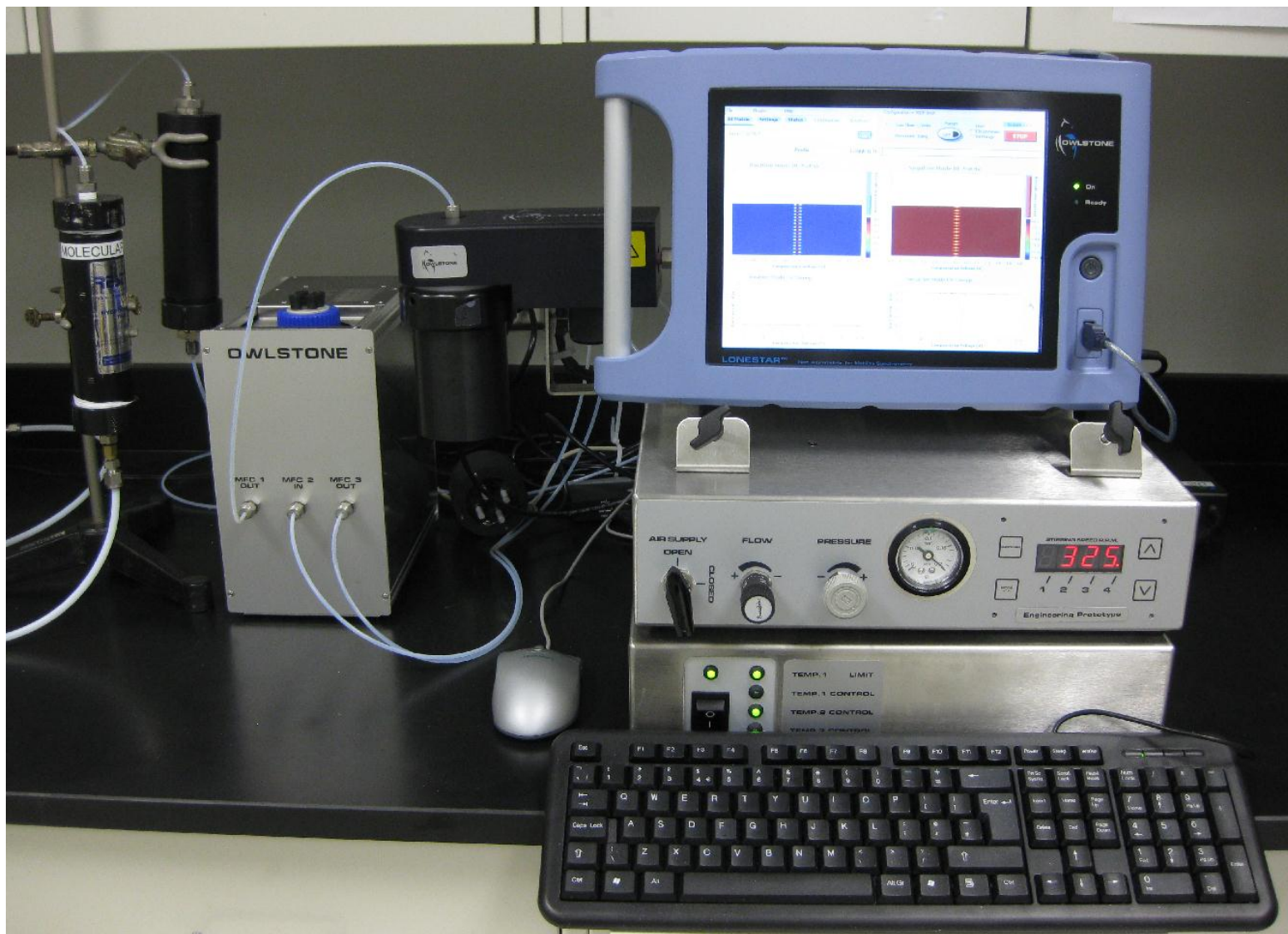
S = Spectrometer

FAIMS = A mass spectrometer without the vacuum but ion mobility not mass to charge ratio.

FAIMS Schematic



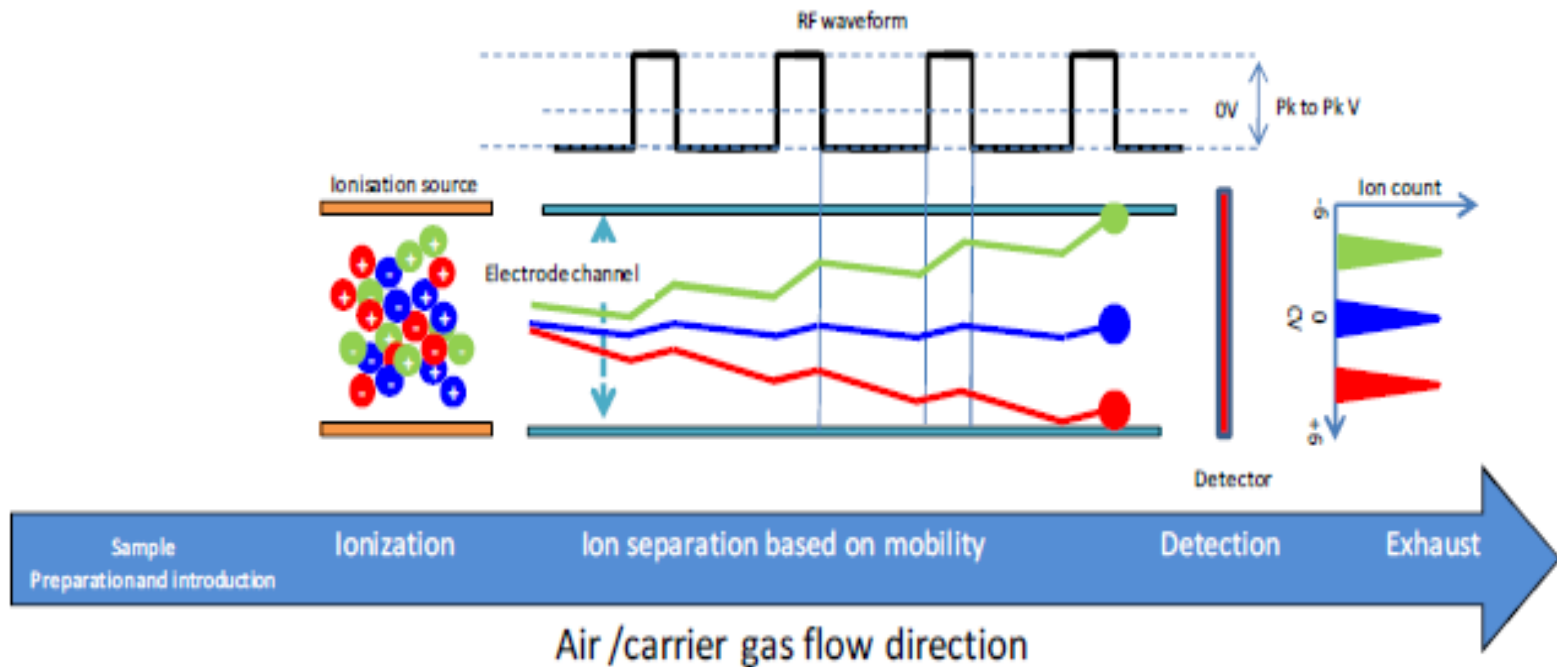
FAIMS



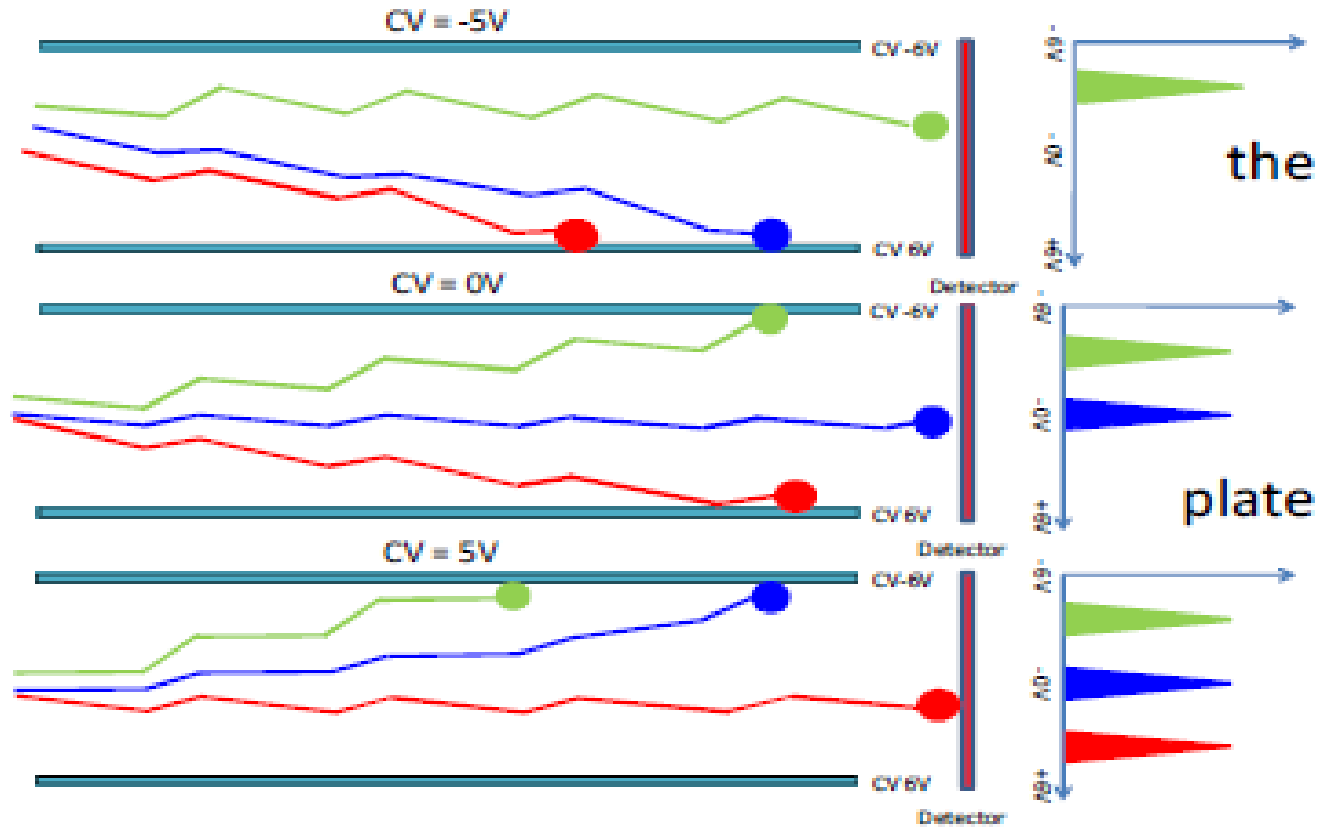
FAIMS Methodology

- Vaporized analyte moves from sample head space through instrument.
- Ionized by Ni⁶³ beta emission source.
- Positive and Negative ions produced.
- Ions enter electrode channel.
- Experience two perturbations.
- RF waveform dispersion voltage (DV) on top plate.
- Compensation voltage (CV) on lower plate.
- Ions are brought to impinge on the detector.
- Ions separated based upon their respective ion mobilities.
- CV spectrum is produced, DF versus CV.
- Ion current (AU) is a measure of concentration.

RF Waveform Dispersion Voltage applied to upper plate



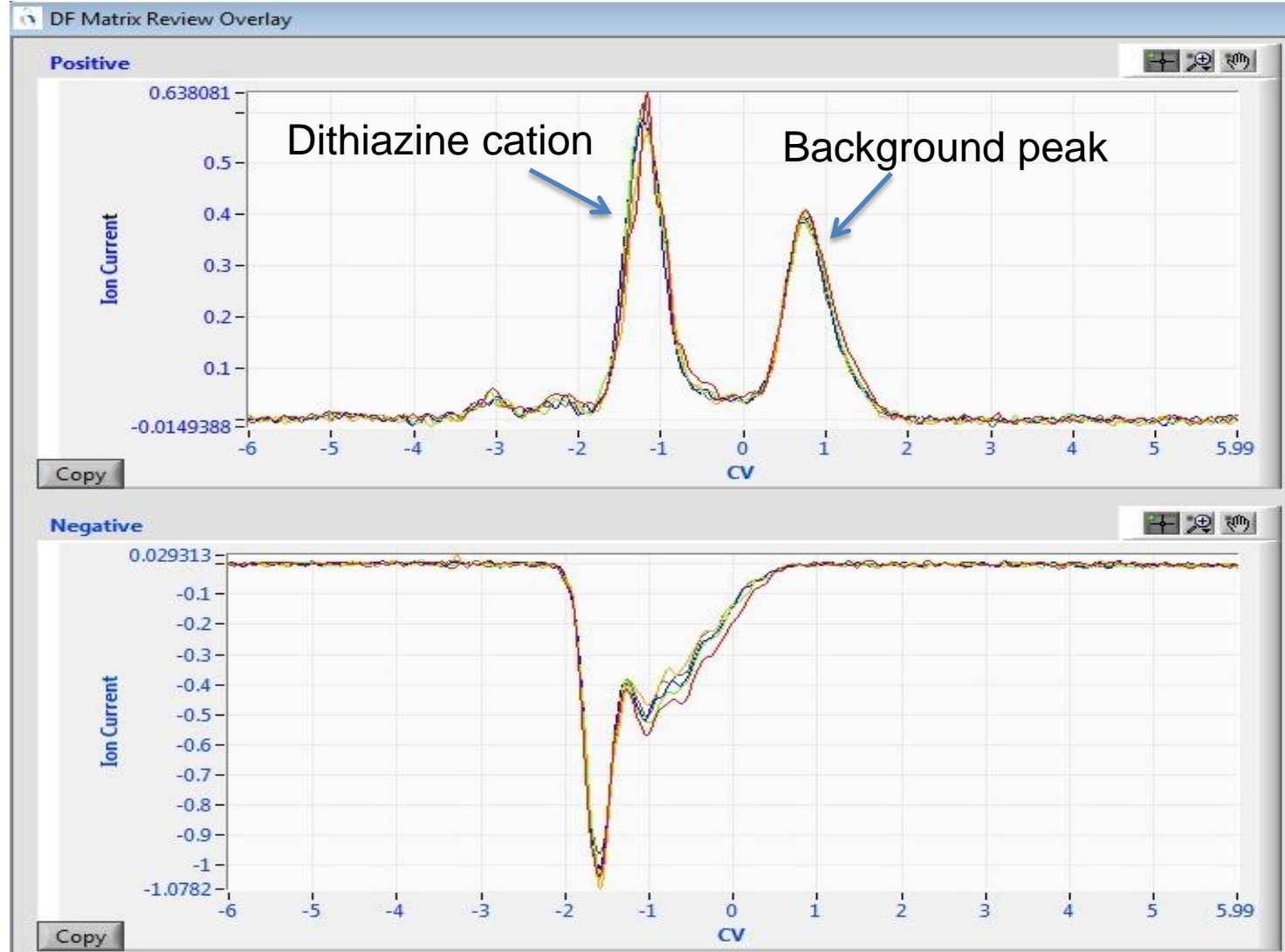
DC Compensation Voltage applied to lower plate



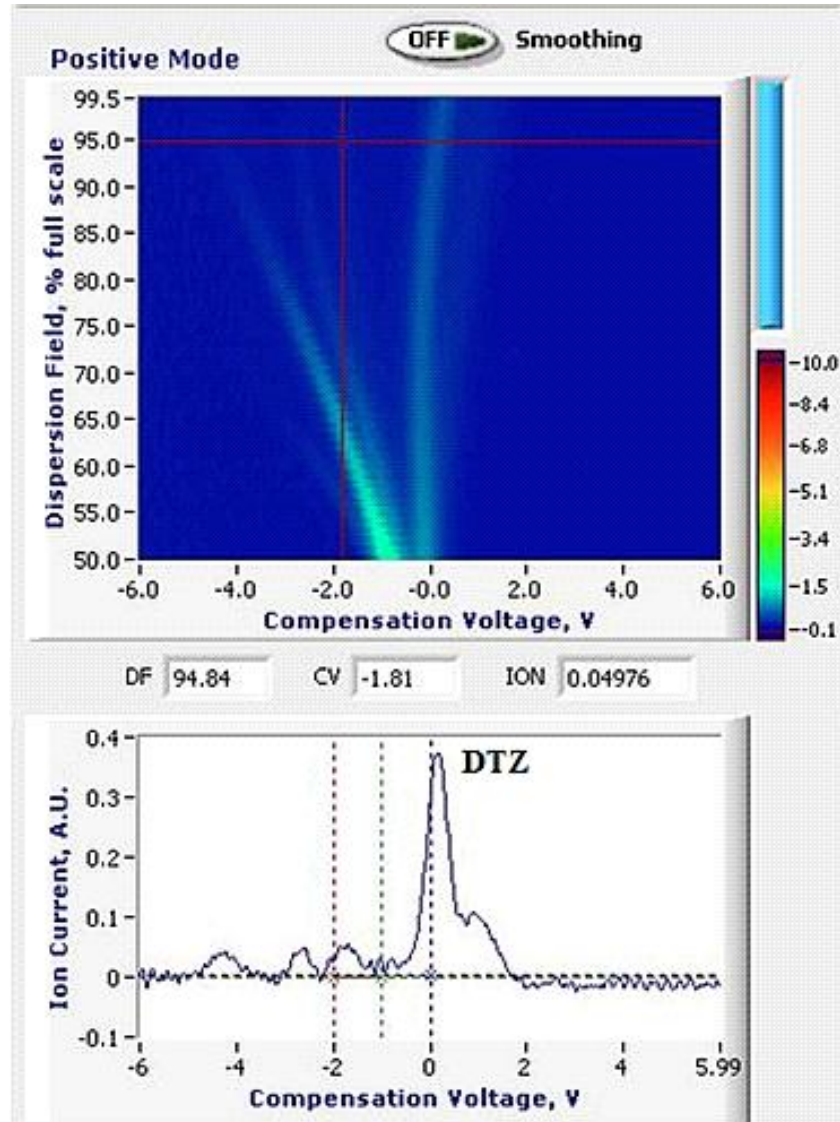
Method Verification

- From Previous work it is known HHTT is detectable.
- Can the FAIMS see Dithiazines?
- 5-Hydroxyethyldithiazine (III) known to be unstable in solution.
- Tested on known stable structural variant of (III).
- Very good reproducibly obtained.
- Initiated development of HHTT and DTZ analysis method in aqueous.

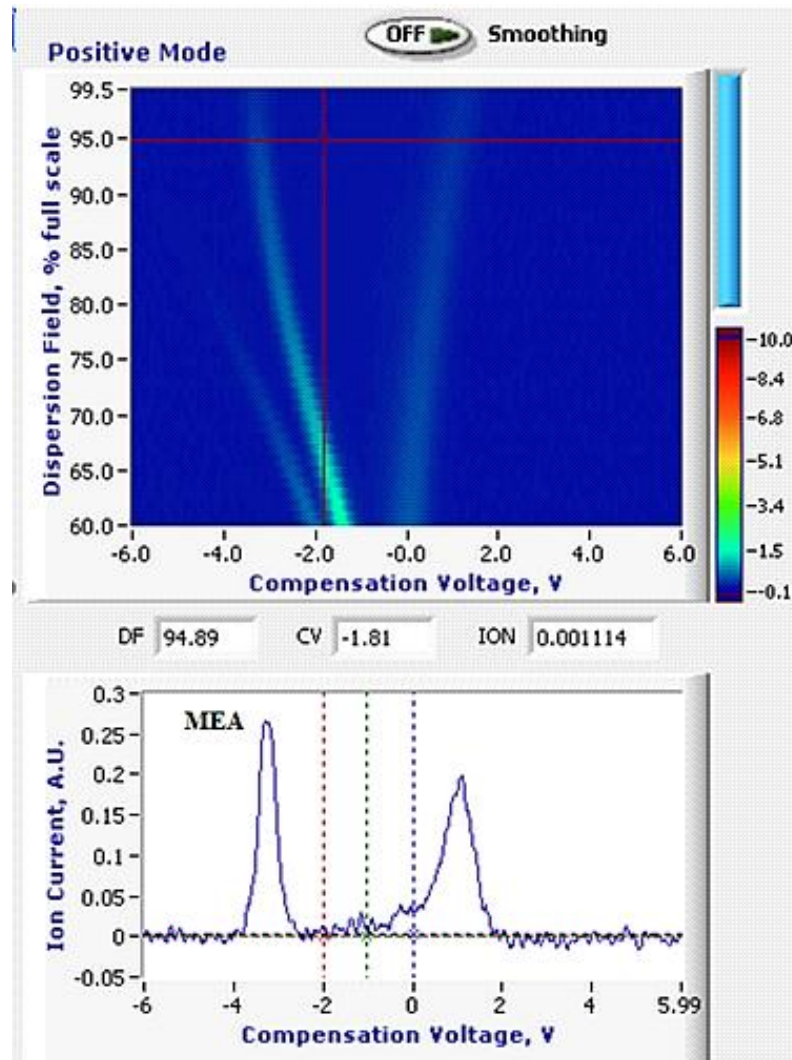
Repeat Samples of a Stable Reference Compound Dithiazine at 100 ppm



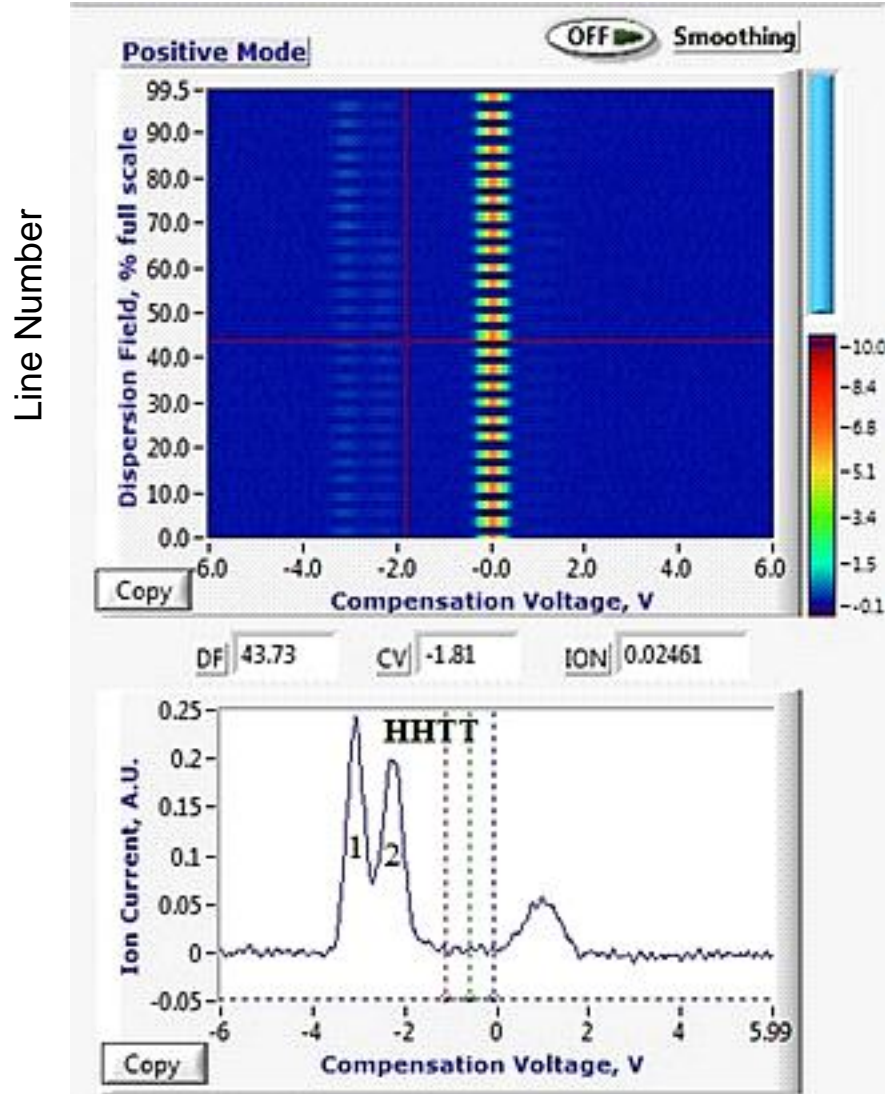
Dithiazine (DTZ) Positive Ion Matrix only



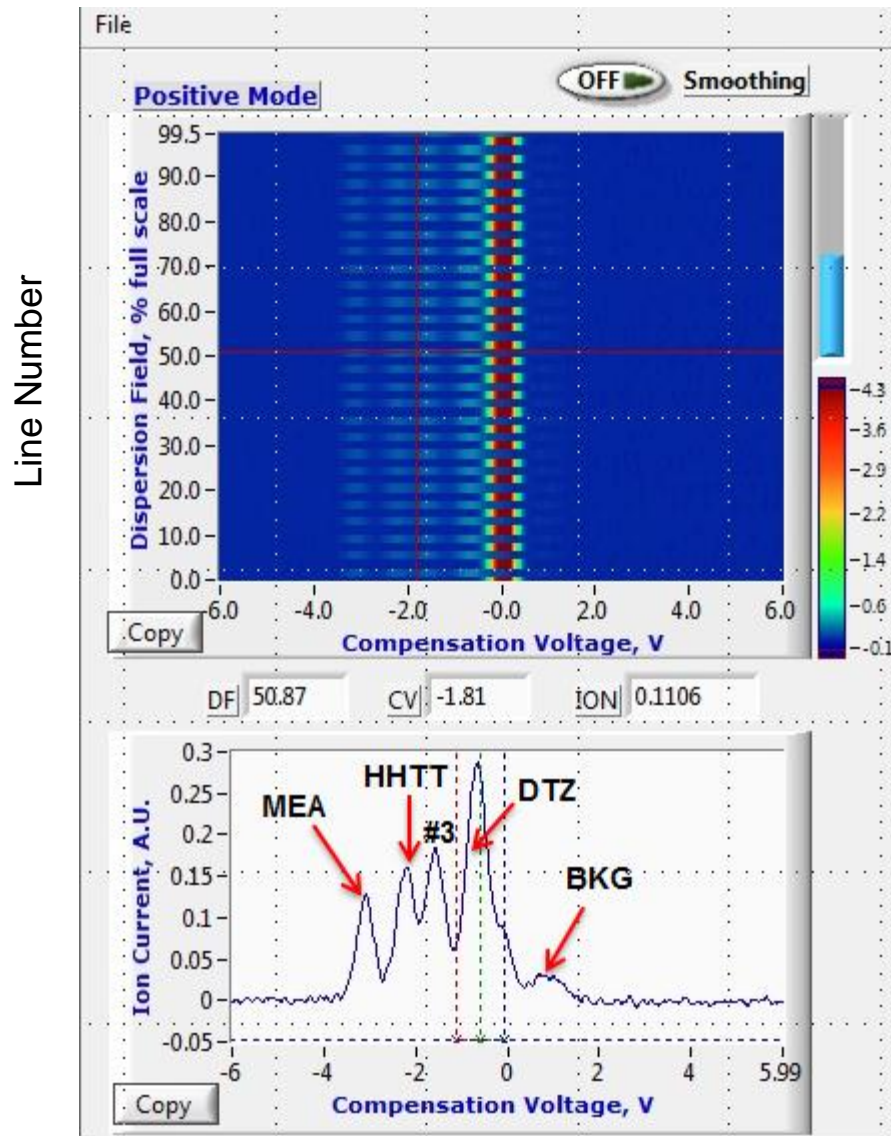
Monoethanolamine (MEA) Positive Ion Matrix only



Hexahydrotriazine (HHTT) Positive and Negative Ion Matrices



Field Sample E - Spent Triazine (HHTT)

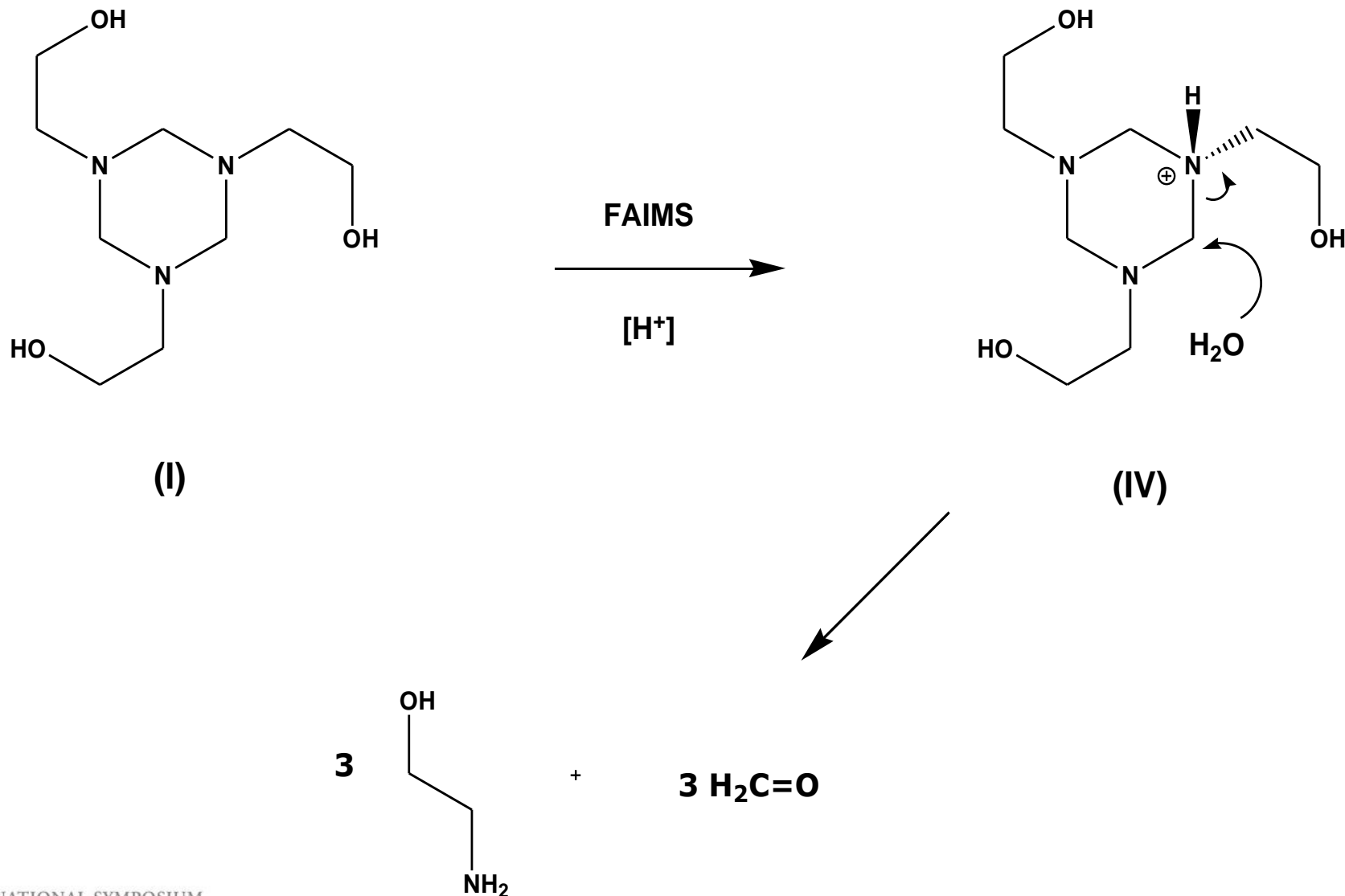


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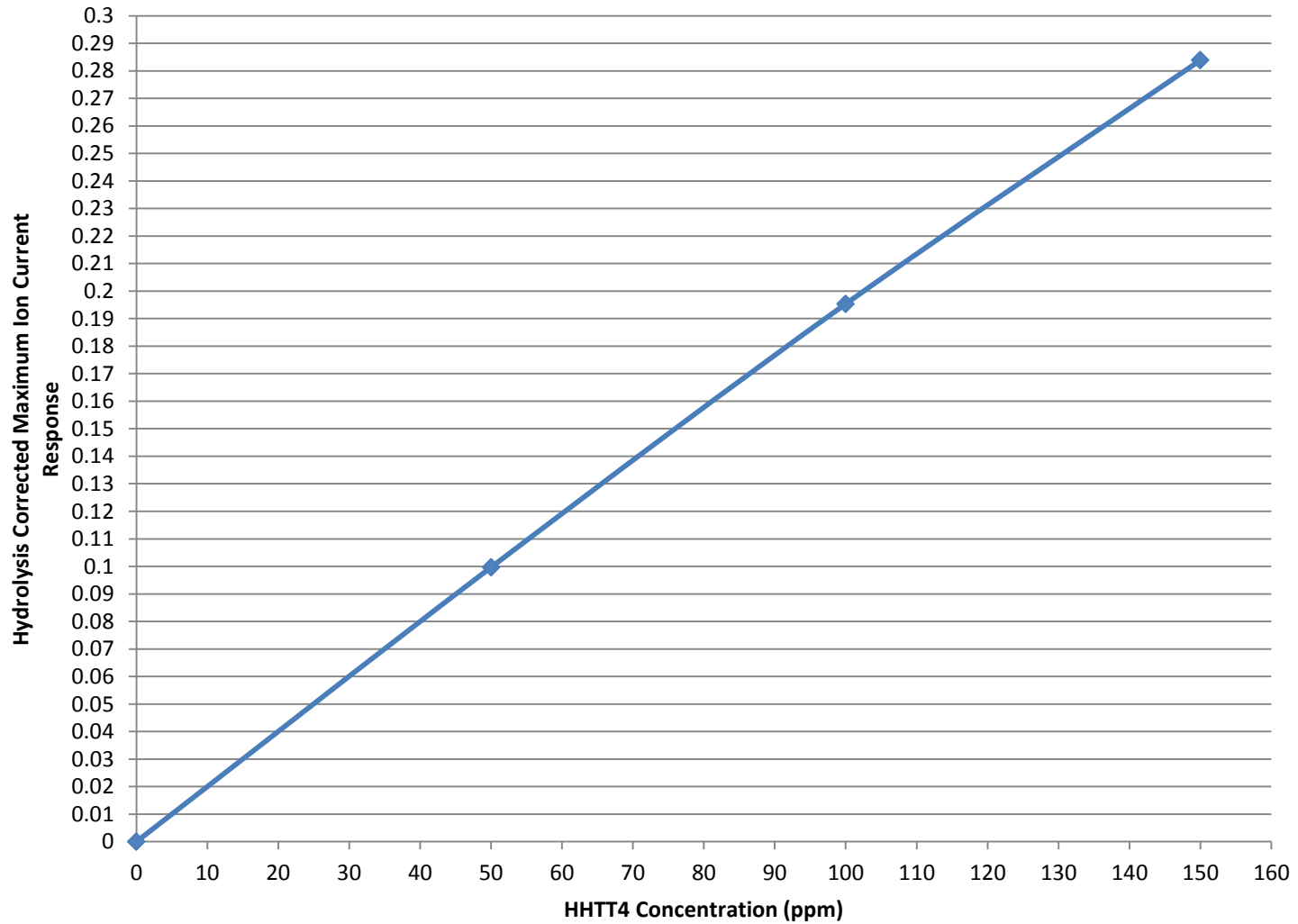
Development Issues and Resolution

<u>Problem</u>	<u>Resolution</u>
DTZ standards have limited stability and can polymerize	Always use fresh solutions
DTZ response is dependent upon HHTT concentration	Determine DTZ response correction factor versus HHTT concentration
DTZ response is somewhat time dependent in data collection	Always use the same matrix #
HHTT does not give a single ionic species in FAIMS	Hydrolysis by-product assigned to MEA
METHODOLOGY UPDATE	
HHTT quantitation affected by hydrolysis	Compensation made to include ion current from both peaks
HHTT hydrolysis correct calibration has linearity limits	Ensure field sample dilutions are within linearity ion current limitations
MEA in field samples comes from two sources a) hydrolysis of HHTT in FAIMS and b) reaction of HHTT with H ₂ S	Spike field sample and determine HHTT hydrolysis correction factor

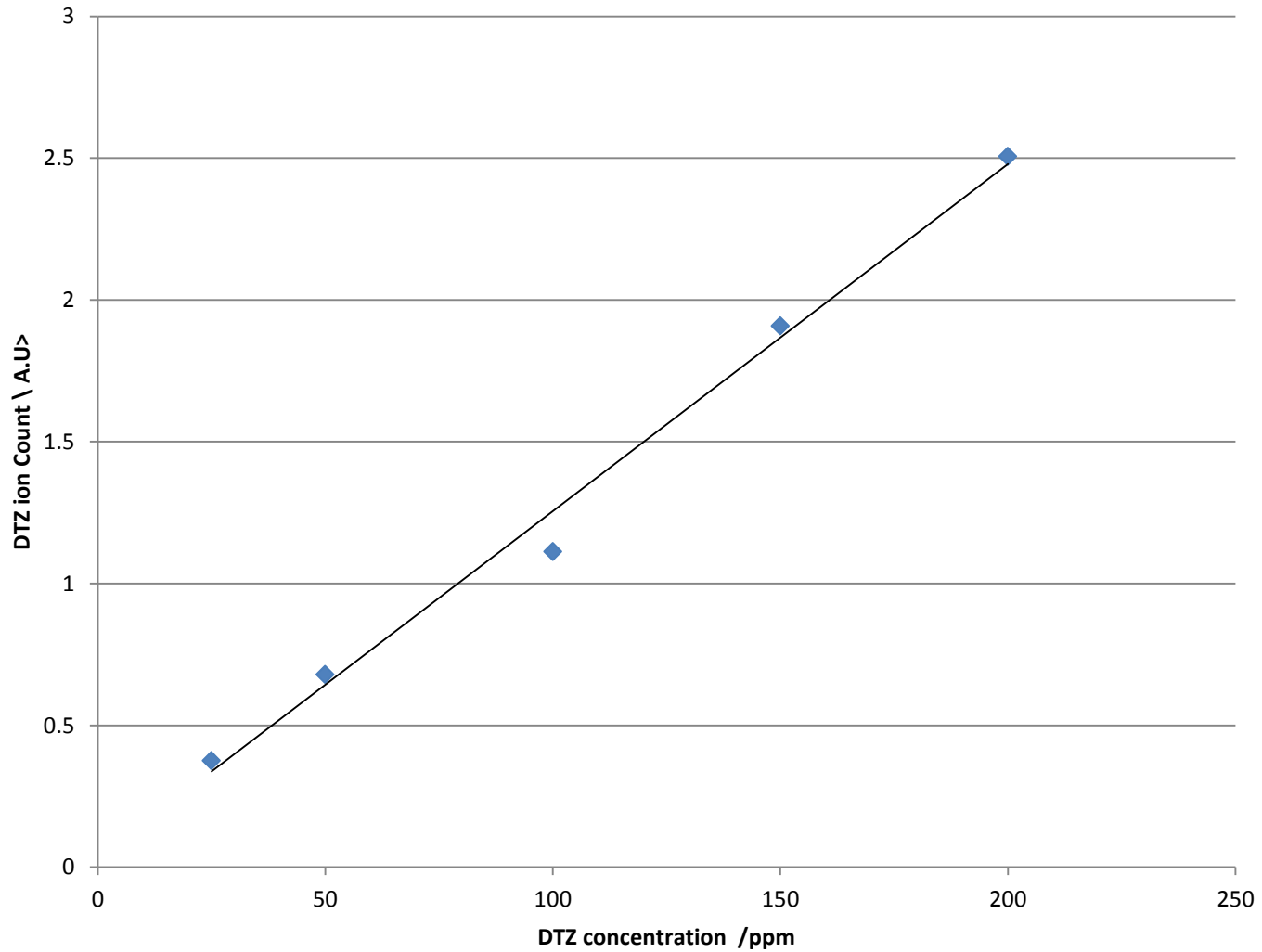
Acid catalyzed hydrolysis of HHTT (I)



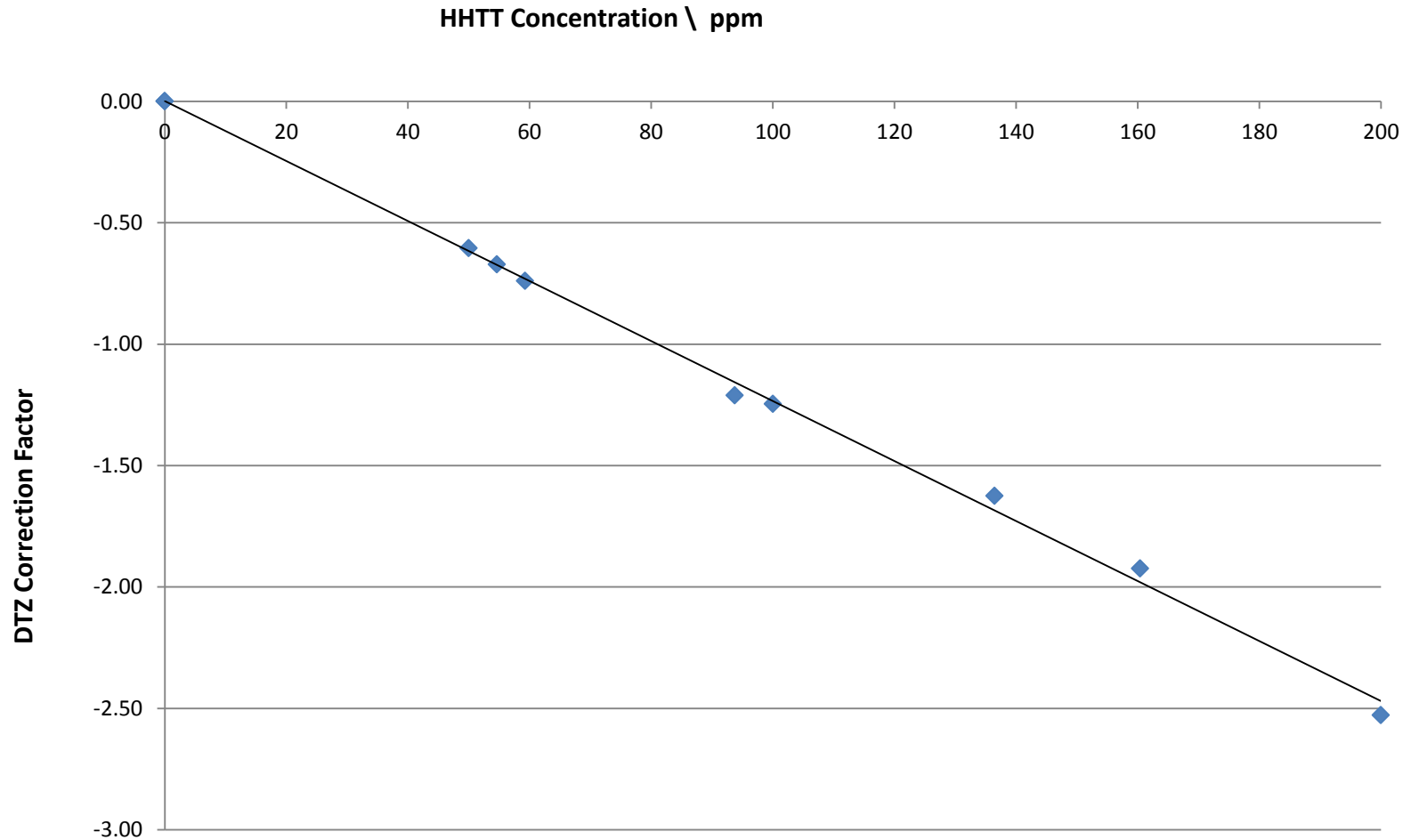
Hydrolysis Corrected HHTT Calibration Curve at 90% Dispersion Field



Dithiazine Calibration Curve at 90% Dispersion Field



Correction factor to Dithiazine Concentration based upon HHTT Concentration



Field Sample Analysis

<u>Field Sample</u>	<u>% Hydrolysis</u>	<u>FAIMS HHTT (ppm)</u>	<u>FAIMS DTZ (ppm)</u>	<u>DEGREE SPENT BY FAIMS (%)</u>	<u>DEGREE SPENT BY GCMS ¹ (%)</u>	<u>Solids</u>
A	77.8	324,000	23,000	6.63		some amorphous dithiazine
B	80.0	50,000	1,000	1.96		crystalline and amorphous solid
C	73.1	100,000	4,800	4.58		lower liquid layer of dithiazine
D	83.1	222,000	21,300	8.75	12.2	no solid, homogeneous fluid
E	80.0	107,496	34,429	31.7	38.0	no solid, homogeneous fluid

1. Gas Chromatographic – Mass Spectrometric Analysis of Chemically Derivatized Hexahydrotriazine-based Hydrogen Sulfide Scavengers: Part II. Grahame N. Taylor and Ron Matherly *Ind. Eng. Chem. Res.* 2010, 49, 6267 – 6269.

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Conclusions

- Current published method requires samples shipped to lab and relatively lengthy process of continuous solvent extraction, chemical derivatization and gas chromatography mass spectrometry analysis.¹
- FAIMS offers a rapid and portable method for spent triazine analysis.
- On site field analysis has been arranged with a customer.
- FAIMS analysis is new technology, and has significant challenges for HHTT/DTZ analysis e.g. mass spectrometer interface to confirm peak assignments.
- Allows optimization use of triazine scavengers.
- Maximize the use of the purchased chemical while avoiding solid deposition.
- The degree spent is a very important parameter in deciding when to empty a static “bubble” tower or optimize a continuous flow type tower.
- Avoid too low level – allows maximum chemical use and prevents wasted \$\$\$\$\$.
- Avoid too high level – risk of solids and difficult/expensive disposal costs.

Acknowledgements / Thank You / Questions

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