

Calibration and Optimization of PTR-MS for Measurement of Methyl Hydroperoxide (CH₃OOH)

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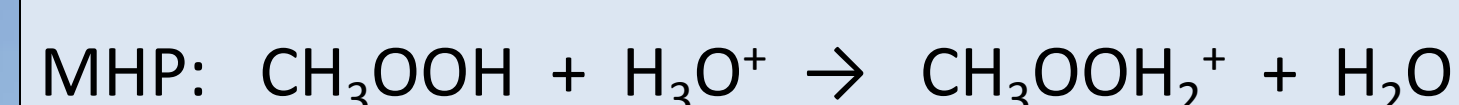


Introduction

Methyl hydroperoxide (MHP) is a major organic hydroperoxide formed in the chain termination reaction between HO₂ and CH₃OO radicals. It is a source of HO_x in the free troposphere through photochemical decomposition into OH. There are few measurement techniques available with the sensitivity to measure this species in air. A promising technique is proton transfer reaction mass spectrometry whereby CH₃OOH is measured using H₃O⁺ chemical ionization. The goal of this research is to optimize and calibrate a Proton Transfer Reaction Mass Spectrometer (PTR-MS) for the analysis of MHP.

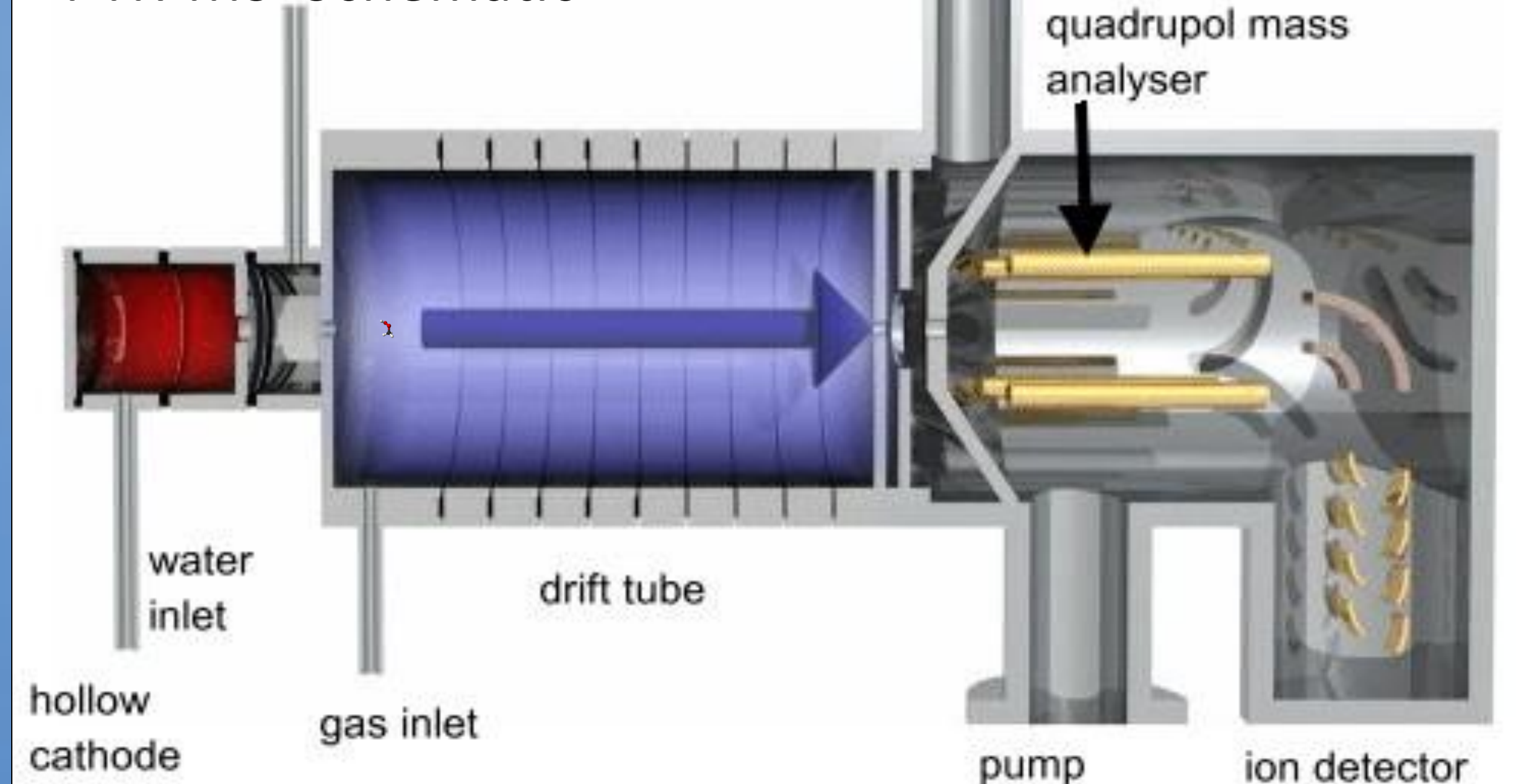
Equipment

The PTR-MS is designed to continuously measure volatile organic compounds in the air. These organic compounds are measured by chemical ionization, whereby the reagent ion H₃O⁺ ionizes organics via a fast proton transfer reaction.



The reaction takes place in a drift tube where the sample air stream reacts with H₃O⁺ ions produced by a hollow cathode ion source. The drift tube is pressure (mbar), temperature (°C), and drift velocity (Townsend) controlled. The protonated organics are mass/charge (m/z) analyzed by a quadrupole mass spectrometer and the ions are counted by a secondary electron multiplier (SEM).

PTR-MS Schematic



Synthesis

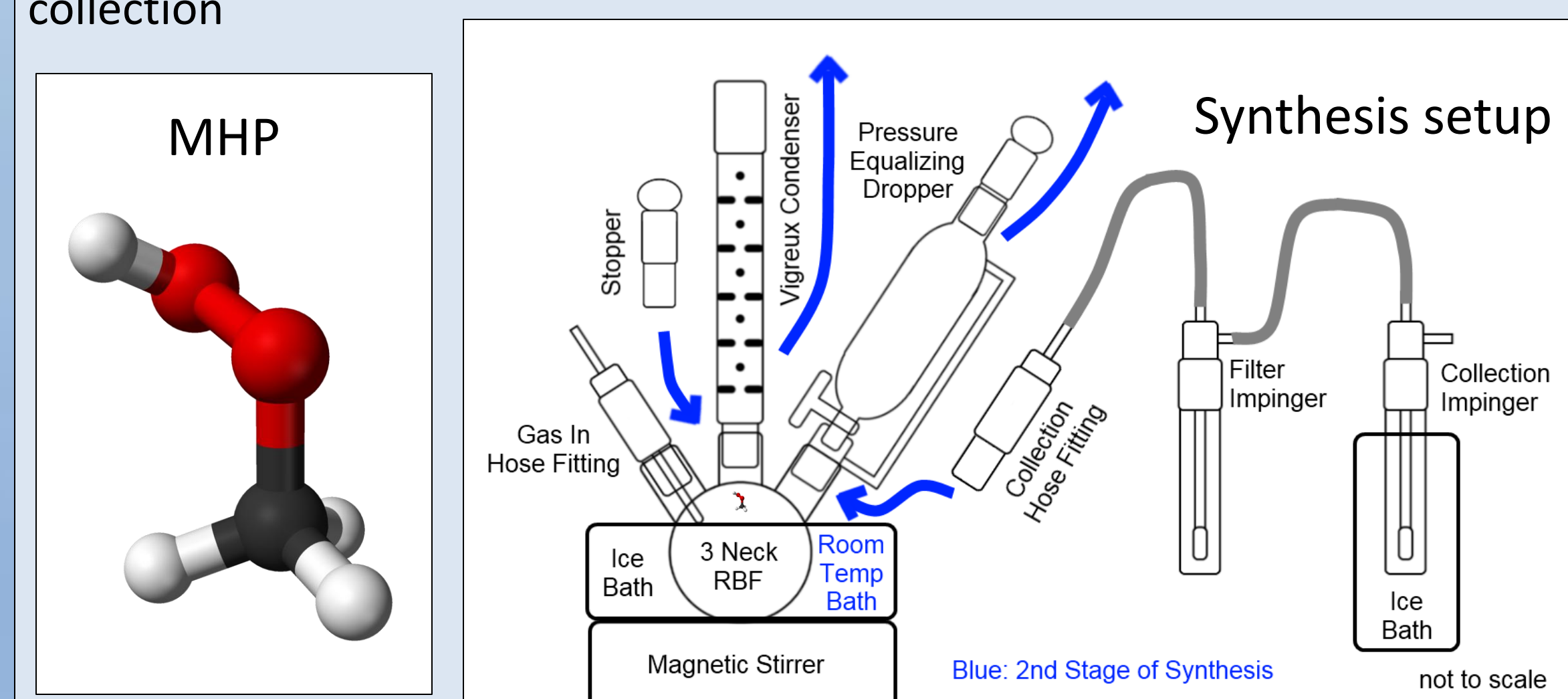
MHP is not commercially available, thus in order to develop a standard for use with the PTR-MS, MHP was synthesized in the lab.

Synthesis:

- Dimethyl sulfate (DMSO₄) and hydrogen peroxide (H₂O₂) were combined in a triple neck round bottom flask (RBF) used as the reaction vessel.
- Nitrogen gas was pumped into the reaction vessel at 15 ml/min to insure that air was not playing a part in the synthesis.
- Potassium hydroxide (KOH) was added drop-wise from a pressure equalizing dropper funnel to the RBF.
- The reaction vessel was submerged in an ice water bath and continuously stirred with a magnetic stirring rod.
- A Vigreux condenser was used to equalize pressure and insure sample wasn't lost.
- Once the reaction was completed, the condenser and the dropper funnel were replaced with stoppers.

Synthesis continued

- A double impinger system was connected to one of the ports on the reaction vessel and nitrogen flow was increased to 30 ml/min.
- The first impinger was kept at room temperature to insure that any H₂O₂ was filtered out.
- The second impinger was kept at approximately 5 degrees Celsius to collect the MHP.
- The temperature differences were to utilize Henry's law for filtration and collection



Method

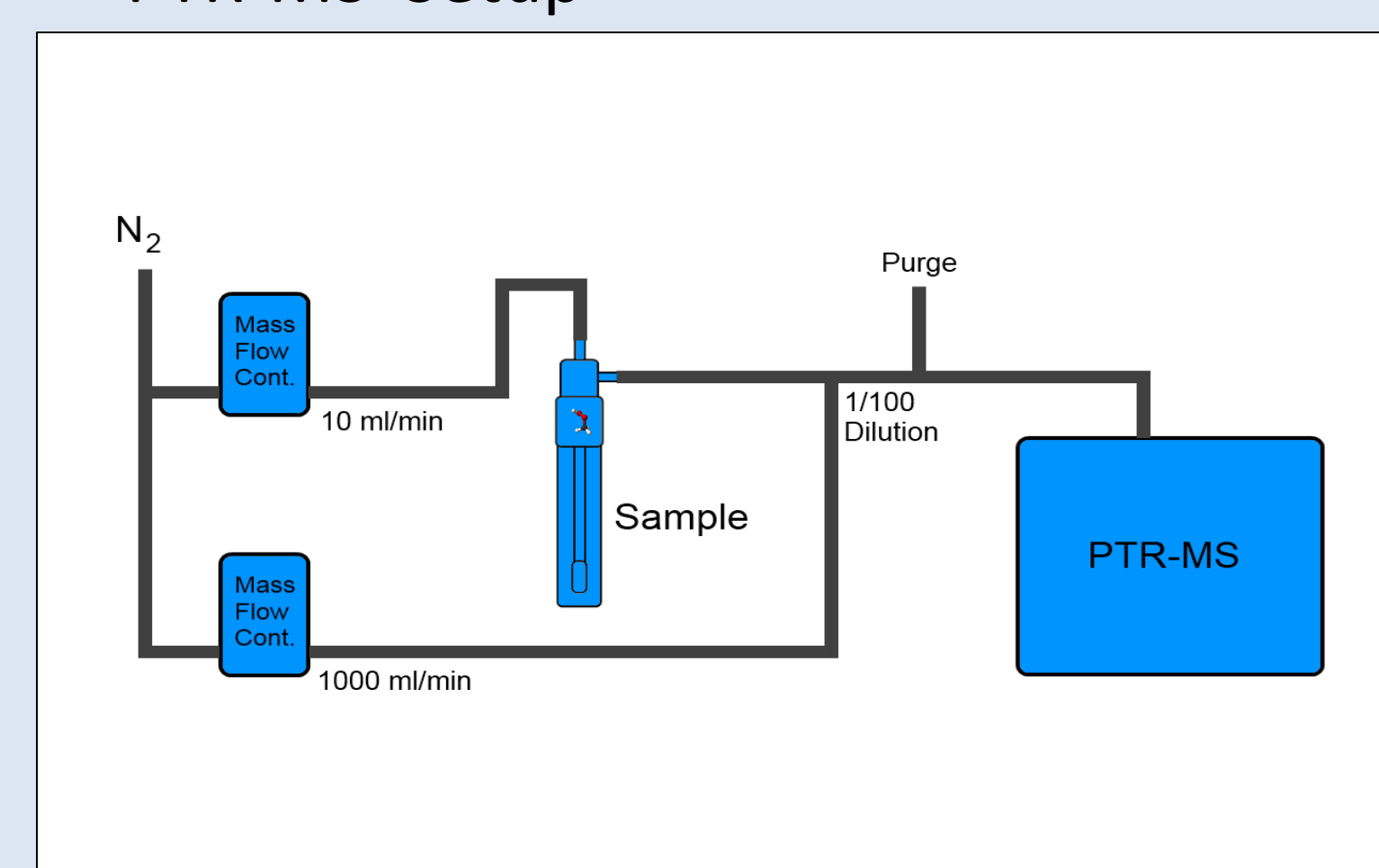
An iodometric titration was performed on the sample to determine the concentration of MHP.

Procedure:

- 10ml of Sample (MHP solution), 10ml of Distilled water, 3ml of 0.05M ferric chloride (FeCl₃•6H₂O), and 5 drops 0.05M sodium iodide (NaI) were mixed in an Erlenmeyer flask and allowed to react for 5 min in the dark.
- 5 drops of Starch indicator (1 wt %) were added
- Performed titration with sodium thiosulfate (Na₂S₂O₃).

To obtain a sample stream for the PTR-MS, 10ml/min of N₂ was pumped through an impinger containing 15ml of sample MHP solution. A 100x dilution flow was connected to the input sample stream to insure that the reaction ion (H₃O⁺) wasn't titrated out.

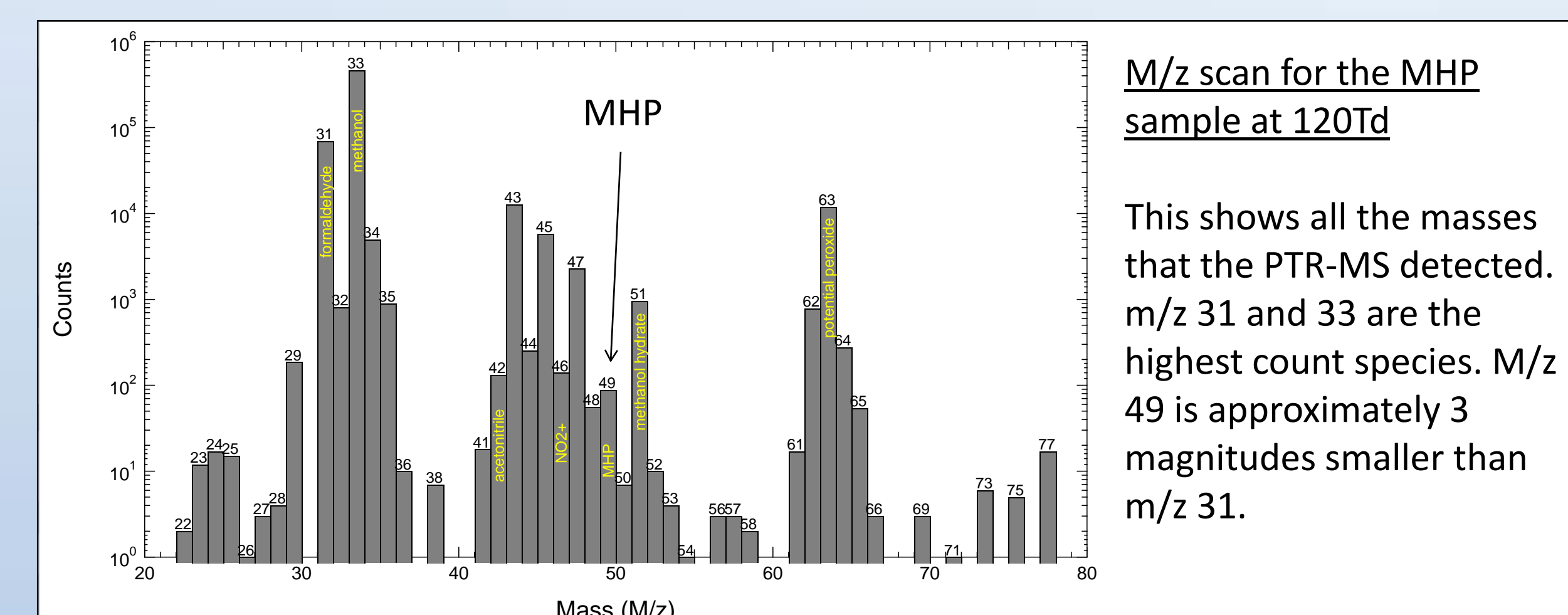
PTR-MS Setup



Discussion/Results

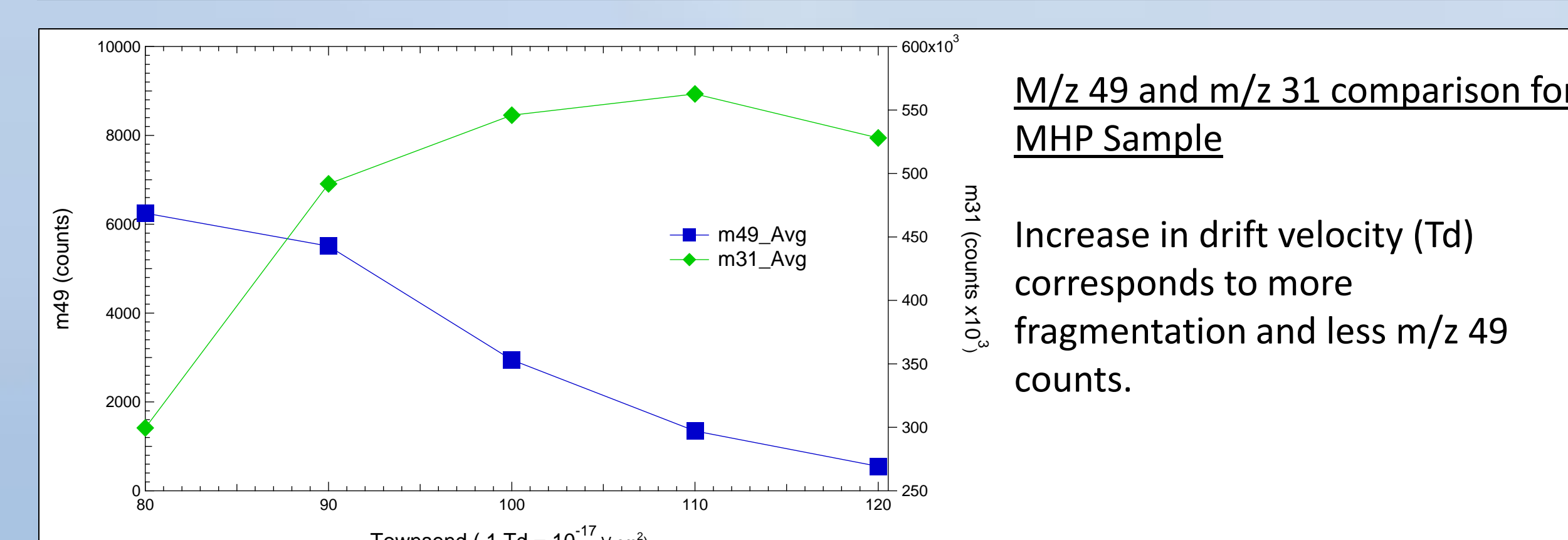
The titration of the MHP sample showed very small concentrations of MHP. The concentration calculated from the titration was approximately 1x 10⁻⁵ M.

Extra species were identified to be the products of likely side reactions in the synthesis of MHP. These other species included excess methanol (m/z 33), formaldehyde (m/z 31), and what appeared to be heavier peroxides such as CH₃OOCH₃ (m/z 63). The PTR-MS measures MHP and formaldehyde as m/z 49 and m/z 31 respectively. In the process of the proton transfer, MHP can fragment to m/z 31 and formaldehyde can form water clusters (HCHO(H₂O)⁺) at m/z 49, so there is an interference between formaldehyde and MHP. From a formaldehyde calibration using ratios of m/z 49 to m/z 49 + m/z 31 at 80 Td, 3.8% of the formaldehyde clustered with water to m/z 49. The MHP sample showed 2000 ppbv of formaldehyde (m/z 31) in the diluted flow! This is a very high concentration of formaldehyde.



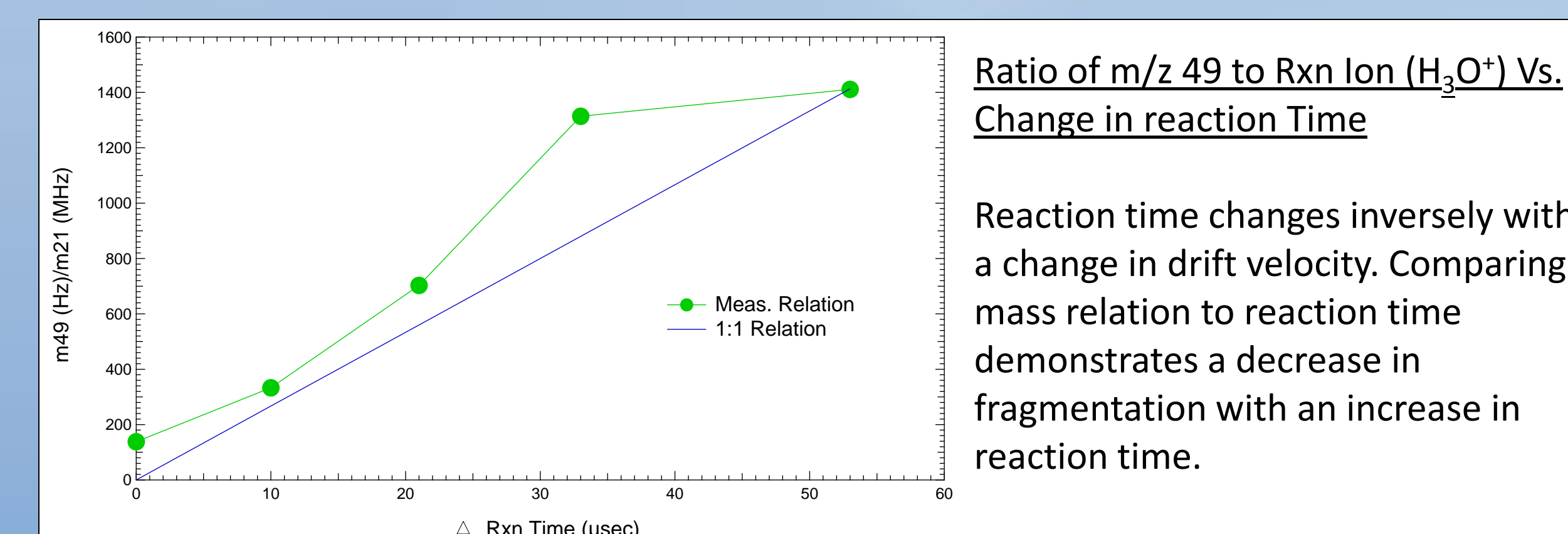
M/z scan for the MHP sample at 120Td

This shows all the masses that the PTR-MS detected. m/z 31 and 33 are the highest count species. M/z 49 is approximately 3 magnitudes smaller than m/z 31.



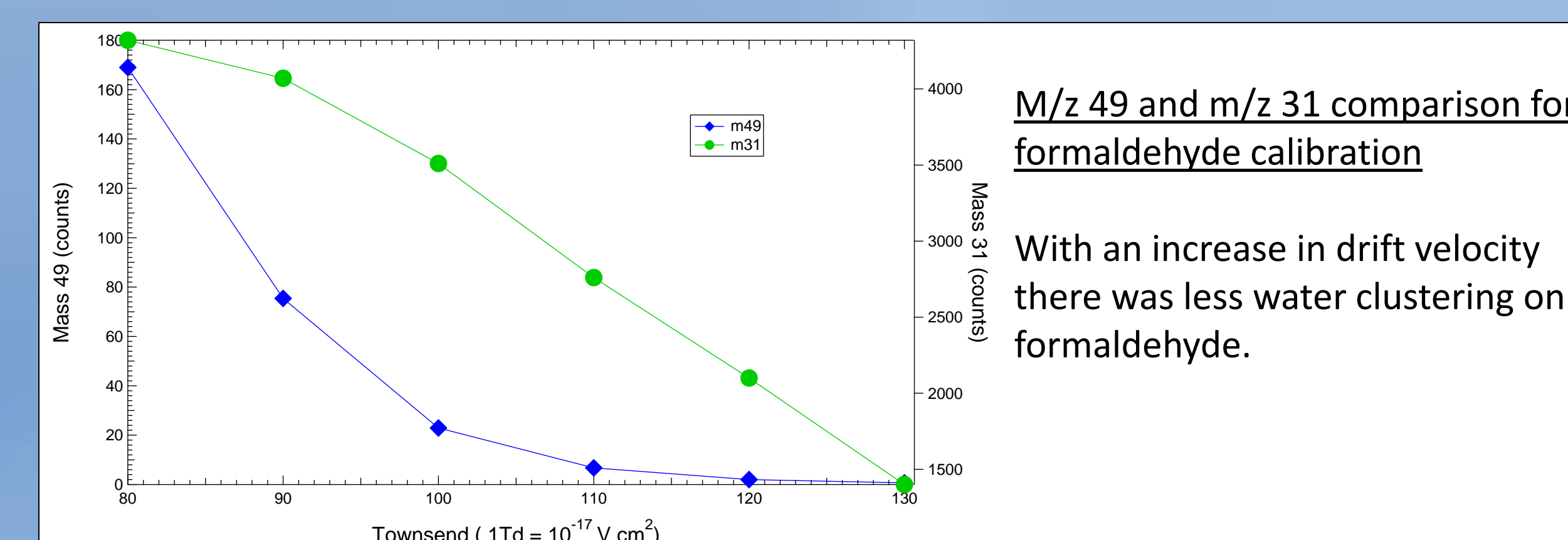
M/z 49 and m/z 31 comparison for MHP Sample

Increase in drift velocity (Td) corresponds to more fragmentation and less m/z 49 counts.



Ratio of m/z 49 to Rxn Ion (H₃O⁺) Vs. Change in reaction Time

Reaction time changes inversely with a change in drift velocity. Comparing mass relation to reaction time demonstrates a decrease in fragmentation with an increase in reaction time.



M/z 49 and m/z 31 comparison for formaldehyde calibration

With an increase in drift velocity there was less water clustering on formaldehyde.

Conclusion

Results from the measurement of a synthesized MHP standard are inconclusive. The mixture contained too many species, in particular formaldehyde, to be useful as a calibration source. Ratios of m/z 49 to m/z 49 + m/z 31 were very low < 5%. This is in agreement with the low concentration of MHP measured by the titration method. What can be concluded is this synthesis will not work for calibrating MHP, due to the interference of other species. A different synthesis technique will need to be implemented to insure that MHP is the major product. The formaldehyde calibration does inform us that a significant amount of formaldehyde (4%) can cluster with water to m/z 49; this will be important in future work for a calibration standard of MHP with the PTR-MS.

References

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