Stephanie H. Kim

Proton Transfer Reaction – Mass Spectrometry (PTR-MS)

Gas chromatography-mass spectrometry (GC-MS)
- Used to detect and quantify gaseous VOCs
- Can achieve sensitivities as low as 0.1 pptV, but...
  (1). takes a relatively longer time for the gas sample components to separate on the column → not very good temporal resolution
  (2). analyte sample needs to be pre-concentrated if the VOCs of interest are present in small concentrations, so that the gases can be detected by instrument [e.g. VOCs are adsorbed onto an adsorbant, then thermally released for column injection and subsequent analysis]
- Summary: GC-MS takes too long (relatively speaking)

PTR-MS
- Uses chemical ionization mass spectrometry, resulting in soft ionization of VOCs (softer, less fragmented ionization method than electron ionization)
- Fast (matter of seconds, even milliseconds), highly sensitive to trace organic gases (in pptV range), real-time on-line measurements and quantifications
- Proton donor (hydronium ion) transfers a proton to VOCs in a gas sample that have a higher proton affinity than water
  -gases in ambient air like N_2, O_2, CO_2, Ar (and most other common inorganic substituents of air) have a lower proton affinity than water → proton transfer does not spontaneously occur b/c not thermodynamically favorable
  -PTR-MS can be used for compounds with lower proton affinity than water, but the method is adjusted and slightly different---O_2^+ and NO^+ reagent ions used instead of H_3O^+
- Ion source, which protonates water, is connected to the drift tube reaction chamber, while gas sample is introduced into drift tube reaction chamber through an air sample inlet; proton transfer between hydronium ions and VOCs occurs in drift tube
  -proton affinity of water = 691 kJ/mol
  -proton affinity of formaldehyde = 713 kJ/mol [only 22 kJ higher than that of water]
- Proton transfer between hydronium ions and formaldehyde has a reaction rate co-efficient of 3 x 10^{-9} cm^3s^{-1} at 300K[1].
  -reverse reaction (de-protonation of H_2COH^+) is temperature and <u>humidity</u> dependent; for the latter, an increase in humidity increases the reverse reaction since water vapor concentration increases [common problem for formaldehyde detection using PTR-MS]
  -presence of other oxygenated compounds (e.g. alcohols like methanol, ethanol) can interfere with formaldehyde, which has m/z = 31
- Formaldehyde is very water-soluble
- The ionized organic species are detected by mass spectrometer (quadrupole-MS or ToF-MS) and separated by mass to charge ratio (m/z) [e.g. for formaldehyde, m/z is 31]
  - $RH^+ = k(\frac{LN}{\mu_0 N_0 E})[R]H_3O^+\varepsilon$
- Length of drift tube (L) and drift velocity α ion reaction time (t); $t = (\frac{LN}{\mu_0 N_0 E})$
- E = electric field/voltage gradient in drift tube per cm; N = buffer gas density of molecules per cm^3
  -generally, low E/N and high drift tube pressure increases PTR-MS sensitivity (for formaldehyde, a higher E/N can limit reverse reaction, but lower E/N has better sensitivity)

-too high E/N = fragmentation problem, but too low E/N = formation of water cluster ions problem
-units for E/N is Townsends (Td); 1 Td = 1 x 10^{-17} V/m^2

Summary of http://www.atmos-chem-phys.net/10/1821/2010/acp-10-1821-2010.pdf

- Potential problems for formaldehyde detection using PTR-MS:
  (1). Reverse reaction (de-protonation) of H_2COH^+ is common b/c proton affinity of formaldehyde (713 kJ/mol) is only slightly greater than that of water (691 kJ/mol)
  -reverse reaction is dependent on *humidity*, temperature, drift pressures, density of molecules (N) in drift tube reaction chamber, and electric field (E)
  (2). At low electric fields (low E/N), water cluster ions form, and side ligand switching reactions between water cluster ions and formaldehyde can occur
- This paper discusses how PTR-MS formaldehyde sensitivity with a low operating E/N (which results in better sensitivity than high E/N) can be improved through sample drying, which involves using a cold trap to remove excess water vapor from the drift tube to mainly reduce de-protonation of H_2COH^+; focuses on one way of addressing the humidity dependence of PTR-MS HCOH sensitivity
- Before sample drying: formaldehyde sensitivities exponentially decreased when water vapor mixing ratios increased and when E/N ratio was decreased (which would increase water cluster ions)
- Sample drying: cold tube water trapping used to remove water vapors from sample stream through condensation; effectiveness of the water trapping system was gauged by using PTR-MS to measure the water cluster ions count rate
  -decrease in abundance of water cluster ions = effective water removal by cold tube trap (determined that water removal was most effective at flow rates <300 ml/min)
  -increase in/high abundance of water cluster ions = ineffective water removal by cold tube trap (determined that water removal was least effective at flow rates >300 ml/min)
  -cold tube trapping could also possibly remove some low vapor pressure organic compounds through their adsorption to the cold tubes
- Results:
  -operation of cold tube trap at lower temperatures increased PTR-MS formaldehyde sensitivity (evident by the decrease in abundance of water cluster ions), but formaldehyde and other organics could also be lost due to their adsorption to the cold tubes or due to ice formation on tubes/liquid water layer on ice surface of the tubes
  -from these results, optimum temperature for water trap determined to be -30°C---not cold enough to result in loss of certain organics to the cold tubes, but not warm enough to have loss of soluble species to water

Sources of Information
(1). http://pubs.acs.org/doi/pdf/10.1021/cr800364q
(2). http://www.epa.gov/region6/qa/presentations11/c11-jor-p.pdf
(3). http://en.wikipedia.org/wiki/Proton-transfer-reaction_mass_spectrometry
(4). http://www.atmos-chem-phys.net/10/1821/2010/acp-10-1821-2010.pdf
(5). http://files.harc.edu/Sites/TERC/About/Events/Other200503/VOCMeasurements.pdf