

*Project H48-2005*

**Aircraft Measurements of Highly Reactive Volatile Organic  
Compounds Using Proton Transfer Reaction Mass Spectrometry (PTR-  
MS) During TexAQS II**

**Final Report**

**Renyi Zhang and Ed Fortner**

**Texas A & M University, College Station, Texas**

**February 15, 2006**

## EXECUTIVE SUMMARY

This project had two primary objectives. The first was to demonstrate that the Ionicon compact proton transfer reaction mass spectrometer (PTR-MS) could be used to gain valuable information regarding the presence and amount of volatile organic compounds (VOCs) over industrial, urban and biogenic sources. Another key objective was to track the evolution of these VOCs dynamically through space and chemically as primary VOCs are converted to oxidation products, particularly in relation to other trace gas (CO, O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>) plumes.

The PTR-MS instrumentation was used during the Southeast Texas Tetroon Study (SETTS) from 17 July - 31 July and the Northeast Texas Plume Study (NETPS) from 1 August - 31 August. The instrument conducted airborne measurements of VOCs during both of these projects flying 5 missions totaling approximately 40 flight hours during SETTS and 11 missions totaling approximately 60 hours during NETPS.

The primary purpose of SETTS was to track the movement of tetroons (balloons) after they had been launched and conduct trace gas measurements of the air mass the tetroon tagged as that air mass moved dynamically through space. Due to convective instability during the daylight hours the decision was made to conduct these flights in the evening. The PTR-MS was able to track the movement of VOCs at night within the tagged air parcel. On the evening of July 26-27 a polluted air mass with elevated mass 43, mass 45 (acetaldehyde) and mass 57 VOCs along with elevated O<sub>3</sub>, CO, and NO<sub>x</sub> was tracked from the Houston metropolitan area to an area northwest of Shreveport LA, a distance of over 200 miles (Fig 10-14). The chemical evolution of this plume was minimal due to the lack of sunlight.

A total of four transects were conducted that sampled polluted Houston ship channel air due to the fact that the primary goal of SETTS was to track tetroons not sample ship channel air. On the flight conducted on the evening of July 21 a pronounced peak of mass 57 which is primarily associated with butenes, octane and MTBE was encountered while conducting a ship channel transect at around 7:30 PM CDT (Fig 4). This peak had a magnitude of 28 ppbv against a background of approximately 500 pptv and the peak lasted for five measurement cycles of the instrument which is a time duration of approximately 50 seconds. On the three subsequent transects of the ship channel conducted on July 26 a smaller mass 57 peak was located in the same general area of the ship channel (Fig 9).

Another VOC finding of interest during SETTS occurred during the evening of July 23 when an overflight of the forested Trinity River Valley at night produced mass 69 (isoprene) and mass 71 (methyl vinyl ketone and methacrolein) peaks of 800 pptv and 8 ppbv respectively. Isoprene is a biogenic VOC and methyl vinyl ketone and methacrolein are its oxidation products. This flight was done at 11:30 PM CDT at 1500' above the valley suggesting the possibility of higher VOC concentrations at a lower altitude and an earlier time during the evening (Fig 7, 8).

The NETPS campaign focused on the emissions from power plants in northeast Texas and attempted to study the evolution of these plumes as they passed through the Dallas metropolitan area. Unfortunately the vast majority of these plumes did not intercept the Dallas area but stayed in rural areas. Power plants do not emit VOCs in general so during these rural flights the primary VOCs of interest were again mass 69 and mass 71 biogenic VOCs found in river valley areas (Fig 19, 20).

Flights were conducted downwind of Dallas on 6 days and generally the only VOC masses which were found to be elevated on these mid to late afternoon flights were mass 43 and mass 45 (acetaldehyde). These masses were not always elevated but when they were they were found within the elevated urban plume of O<sub>3</sub> and CO or just to the side of it (Fig 17, 18).

In summary the compact PTR-MS was able to locate, quantify and track the movement of VOC plumes associated with industrial, urban and biogenic sources. Tracking chemical evolution of VOCs was limited by the lack of chemical evolution during evening flights and the lack of flights originating in a high VOC area such as the Houston ship channel area during the daytime which could then track evolution of VOC plumes. While these flights succeeded as a demonstration of the PTR-MS ability they did not produce a substantial statistical database for any of the findings mentioned above. A future study which focused more exclusively on one aspect of these findings will probably yield more statistically relevant results. This study could be focused on any one of the following; ship channel emissions of VOCs, tracking the chemical evolution of ship channel emissions of VOCs during the daytime, studying the contribution of VOCs to the downwind of Dallas urban plume (or any urban plume for that matter) during the daytime and finally a study of biogenic VOCs in forested river valley areas and any plumes associated with them.