

**James Sweet**

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**From:** Allen Goldstein [ahg@nature.berkeley.edu]  
**Sent:** Thursday, May 05, 2005 9:24 AM  
**To:** J.P. Cativiela  
**Cc:** holzing@nature.berkeley.edu; slshaw@nature.berkeley.edu; FMMitloehner@UCDavis.Edu; Bill Descary (E-mail); Carolina Simunovic (E-mail); Dave Warner; David Grantz (E-mail); Deanne Meyer (E-mail); Denise Mullinax (E-mail); Diane Bailey (E-mail); J. P. Cativiela (E-mail); James Sweet; John Watson (E-mail); Kevin D. Hamilton (E-mail); Paul Martin (E-mail)  
**Subject:** Re: FW: questions

JP,

Stephanie Shaw, Rupert Holzinger, and I have prepared answers to your questions. We tried hard to be complete and clear, but I realize some of the answers might be a bit more technical than you need. I hope this information is useful to DPAG.

-Allen

>> 1 - In the attached document, "Compromise EF for Dairies 2", prepared by  
 >> David Warner of the air district, he characterizes the capabilities of  
 >> PTRMS as described by you as follows: "Dr. Goldstein, who performed the  
 >> PTRMS measurements, previously indicated to DPAG that PTRMS measures  
 >> oxygenated VOCs, but would not effectively measure amines, which are not  
 > oxygenated, or volatile fatty acids or phenols, which are difficult to  
 > collect through sampling tubes." Is this an accurate characterization in  
 >> your view?

>  
 Proton transfer reaction mass spectrometers use a chemical ionization method in which H<sub>3</sub>O<sup>+</sup> ions are allowed to react with a gaseous sample. If a given compound in the sample has a proton affinity greater than that of water, the proton is transferred to the compound, which can then be detected. Many classes of VOC have proton affinities larger than that of water (166.5 kcal/mol), including alcohols, aldehydes, aromatics, ketones, alkenes, nitriles, sulfides, and acids.

Oxygenation of the target compound is not a requirement for detection. For examples of proton affinities, please see the following references:

W. Lindinger, A. Hansel, and A. Jordan, (1998) Proton-transfer reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels, *Chemical Society Reviews*, 27, 347-354.

Lias, S.G., Bartmess, J.E., Liebman, J.F., Holmes, J.L., Levin, R.D., and Mallard, W.G. (1988) Evaluated gas-phase basicities and proton affinities of molecules - heats of formation of protonated molecules, *J. Phys. Chem. Ref. Data*. 17 and subsequent software updates.

Zhao, J, R. Zhang (2004) Proton transfer reaction rate constants between hydronium ion (H<sub>3</sub>O<sup>+</sup>) and volatile organic compounds, *Atmospheric Environment*, 38, 2177-2185.

We do not have experience measuring the amines, and we were not set up to test for and calibrate measurements of amines. However we did find this paper in the literature, which claims to see dimethyl- and trimethylamine~ also deGouw et al., 2003 report them

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<http://www.copernicus.org/EGU/acp/acp/5/373/acp-5-373.pdf>

Volatile fatty acids, phenols, peroxides, and peroxyacetylnitrate may have a tendency to condense or be adsorbed by many of the materials typically used in sampling lines prior to the PTRMS inlet. Therefore, these compounds often can only be detected if at sufficiently high concentrations, and then only qualitatively, as these loss processes often do not occur at correctable rates. However, this needs to be tested for each experimental setup. For example, with the Goldstein lab setup during the UC Davis 2004-2005 chamber experiments we detected masses that could indicate emissions of acetic acid and phenol when the cows were present, but at extremely low amounts. Acetic acid was simultaneously measured through a cartridge trapping method by collaborators from Iowa State. Their results indicate high concentrations of acetic acid, which is consistent with the fact the PTRMS was able to detect it at all.

Please note that the PTRMS can indeed quantitatively detect dimethylsulfide and dimethyldisulfide, and is likely to be able to detect a large range of other sulfur-containing compounds, but not carbon disulfide. However, to our knowledge few of these compounds have been calibrated on the PTRMS thus far.

It is possible that individual compounds might not be detectable by PTRMS, even if their class typically is detectable. This is the case for ethanol during our work at UC Davis. Instead of being detected at mass 47 (molecular weight +1), ethanol is converted to an unstable fragment at mass 29 amu fragment which cannot be detected. However, it may be possible to detect ethanol in future experiments depending on the parameters chosen for control of the ionization source.

>> 2 - Specifically, are phenols "difficult to collect through sampling tubes" or would the PTRMS otherwise fail to measure them?

Phenol (C<sub>6</sub>H<sub>5</sub>OH) can be detected by PTRMS, although the issues prior to injection in the PTRMS, as well as fragmentation due to the OH moiety present, as described above mean that the signal can be quite small, even for relatively high concentrations in the sample stream. For the Goldstein lab setup at UC Davis, we were able to detect phenol emissions in the chamber when the cows were present. In addition, we calibrated this gas and found good recovery of our standard, which will result in quantifiable emission rates. Larger molecular weight phenols probably will have more issues with sticking in the inlet system than C<sub>6</sub>H<sub>5</sub>OH did.

>> 3 - I have found some indications in the literature that certain compounds which appear to be amines (Trimethyl amine) are recorded by PTRMS. Is it accurate to state that amines are not captured?

Amines have high proton affinities; thus they are ionized and detected if they are not lost in the inlet system. However, some issues make it hard to measure amines: e.g. at mass 46 (protonated dimethylamine) the signal to noise ratio is very poor due to contamination from the ion source, and protonated trimethylamine is detected at the same mass (60 amu) as acetone with one <sup>13</sup>C atom which reduces the chance to detect small amounts of the compound.

> - Warner (see below answers #1 and #2) identifies several compounds, including toluene, p-xylene, 1,2,4 trimethylbenzene and 1,3,5

- >> trimethylbenzene as not being captured by PTRMS because they are
- >> non-oxygenated. Is he correct in this statement? Are any or all of these
- >> compounds expected to be captured by PTRMS? Also, is there a list anywhere  
or other method to determine whether these compounds have a proton
- >> affinity higher than water?

No, as mentioned above, oxygenation is not a requirement for detection. Toluene and all xylene isomers are detected with a clear, quantifiable signal on the PTRMS. Proton affinities have been calculated from first principles for 1,2,4 and 1,3,5 TMB (Zhao & Zhang, 2004), and there are several reported measurements of these compounds in ambient air samples (i.e. deGouw et al., 2003). We do not yet know if we see a signal at 121amu (signal for TMB compounds) for the UC Davis chamber experiment. Please see the publications mentioned earlier, and the references within, for further proton affinity information.

At 02:16 PM 4/29/2005, you wrote:

Dr. Goldstein:

Thanks for speaking with me the other day. I have some follow-up questions for you. I'm putting them in an email to give you time to consider before answering, if needed. However, if you would prefer to answer via phone that would be just fine with me. I can be reached at any time at 916-261-6556.

Here are the questions:

**1 - In the attached document, "Compromise EF for Dairies 2", prepared by David Warner of the air district, he characterizes the capabilities of PTRMS as described by you as follows: "Dr. Goldstein, who performed the PTRMS measurements, previously indicated to DPAG that PTRMS measures oxygenated VOCs, but would not effectively measure amines, which are not oxygenated, or volatile fatty acids or phenols, which are difficult to collect through sampling tubes." Is this an accurate characterization in your view?**

**2 - Specifically, are phenols "difficult to collect through sampling tubes" or would the PTRMS otherwise fail to measure them?**

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**4 - Warner (see below answers #1 and #2) identifies several compounds, including toluene, p-xylene, 1,2,4 trimethylbenzene and 1,3,5 trimethylbenzene as not being captured by PTRMS because they are non-oxygenated. Is he correct in this statement? Are any or all of these compounds expected to be captured by PTRMS? Also, is there a list anywhere or other method to determine whether these compounds have a proton affinity higher than water?**

--J.P. Cativiela  
Program Coordinator, Dairy CARES