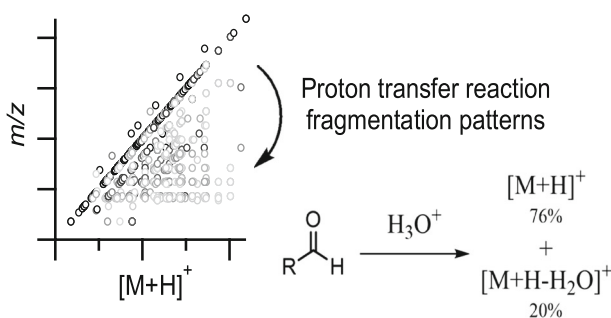


# A Library of Proton-Transfer Reactions of $\text{H}_3\text{O}^+$ Ions Used for Trace Gas Detection

Demetrios Pagonis,<sup>1</sup>  Kanako Sekimoto,<sup>2</sup> Joost de Gouw<sup>1</sup>

<sup>1</sup>Cooperative Institute for Research in Environmental Sciences & Department of Chemistry, University of Colorado, 216 UCB, CIRES, Boulder, Colorado 80309, USA

<sup>2</sup>Yokohama City University, Yokohama, Japan



**Abstract.** We have collected data on the proton-transfer reactions with  $\text{H}_3\text{O}^+$  ions for trace gas detection into an online and publicly available library. The library allows users of proton-transfer-reaction mass spectrometry (PTR-MS) and selected-ion flow-tube mass spectrometry (SIFT-MS) to look up at which  $m/z$  a trace gas of interest is detected. Vice versa, the library also allows looking up what trace gas may have been responsible for a product ion detected in PTR-MS

and SIFT-MS. Finally, the library may serve as a dataset for further research on calculating instrument sensitivity and product-ion fragmentation, improving identification and quantification of newly detectable compounds as advances in instrumentation continue. To demonstrate the utility of the library, we present a brief analysis of product-ion fragmentation. We show that oxygenated organic compounds exhibit trends in neutral loss according to their functionality, and that on average neutral losses decrease the carbon number and increase the extent of unsaturation of product ions.

**Keywords:** PTR-MS, SIFT-MS, Proton transfer reaction

Received: 29 January 2019/Revised: 9 March 2019/Accepted: 10 March 2019/Published Online: 29 April 2019

## Introduction

Chemical ionization using proton-transfer-reactions with hydronium ions ( $\text{H}_3\text{O}^+$ ) is widely used for trace gas detection in air. Both proton-transfer-reaction mass spectrometry (PTR-MS) [1] and selected-ion flow-tube mass spectrometry (SIFT-MS) [2] instruments use  $\text{H}_3\text{O}^+$  ions for ionization and allow online measurements of a wide range of trace gases in air with high sensitivity, fast time response, and without the need for pre-concentration and sample treatment. These techniques have proven useful in a variety of research applications including atmospheric chemistry, plant studies, food science, and medical applications [3–6].

In PTR-MS, a discharge provides a bright source of  $\text{H}_3\text{O}^+$  ions, and the proton-transfer reactions take place at enhanced collision energies to avoid cluster ion formation. Recent instrument developments have improved the sensitivity of PTR-MS and the resolving power of the mass analyzers used [5–8], vastly increasing the number of VOCs that can be detected in different air samples.

In SIFT-MS,  $\text{H}_3\text{O}^+$  ions produced in the source are mass selected by a quadrupole mass filter and react in a flow tube at lower collision energies. Cluster ion formation is avoided by diluting the sample gas in helium. Due to ion losses caused by the additional mass filter in between the source and the flow reactor, the reagent ion signal and thus the sensitivity of SIFT-MS is less than that of PTR-MS. In contrast, the ion source produces no unwanted reagent ions, which makes the mass spectra easier to interpret, and the lower collision energies reduce product-ion fragmentation compared with PTR-MS. The reagent ion employed in SIFT-MS can also be switched rapidly, allowing for analysis of a single sample by multiple reagent ions.

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s13361-019-02209-3>) contains supplementary material, which is available to authorized users.

Correspondence to: Joost de Gouw; e-mail: joost.degouw@colorado.edu

The large number of compounds that can be detected by PTR-MS and SIFT-MS also provides a challenge to the quantification of trace gases. Calibrations using diluted standard mixtures or other methods have typically been used to determine instrument sensitivity. However, accurate calibrations for hundreds to thousands of trace gases are very time consuming and alternative methods need to be considered. In principle, instrument sensitivity can be calculated from the reaction rate coefficients and the collision conditions in the reactor [4]. Rate coefficients have not been measured for all trace gases; however, and in PTR-MS, they need to be known at the elevated collision energies used in the reactor. Rate coefficients can be estimated from the polarizability and dipole moment of the trace gas [9]. The latter are also not known for all trace gases and can be further estimated from the molecular mass and the presence of specific functional groups empirically [10]. In addition, product-ion fragmentation is a large uncertainty in calculating sensitivity and has not been systematically studied.

There is an extensive and growing body of literature on the detection of different trace gases by PTR-MS and SIFT-MS using proton-transfer reactions with  $\text{H}_3\text{O}^+$  ions. In this work, we have collected the existing information in an online, publicly available library. The library allows users of PTR-MS and SIFT-MS to look up at which  $m/z$ 's trace gas of interest is detected and, vice versa, which trace gas may have been responsible for a detected product ion. The library developed in this work can also serve as a dataset to study instrument sensitivity and product-ion fragmentation using, for example, linear regression and machine learning techniques. To illustrate this potential, a few analyses of product-ion fragmentation are presented here. Further growth of the library is anticipated, and users are encouraged to submit their peer-reviewed data for this purpose.

## Methods

An online, publicly viewable Google Sheet ([www.tinyurl.com/PTRLibrary](http://www.tinyurl.com/PTRLibrary)) was created using data from 49 publications [1, 4, 11–58] and currently contains nearly 1000 entries of different trace gases detected by PTR-MS and SIFT-MS. The library as it exists at the time of this publication has been included as electronic supplementary material of this paper. The information contained in the sheet consists of the following:

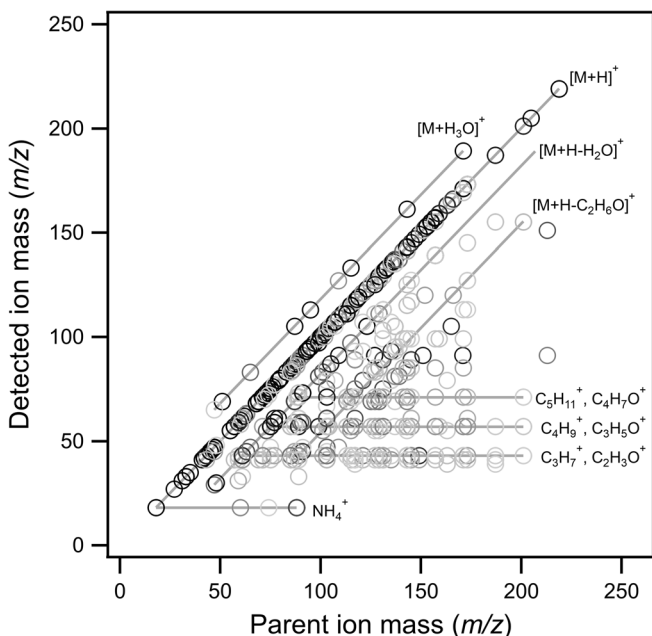
1. Compound identifiers: The protonated ion mass  $[\text{M}+\text{H}]^+$  is used as a leading identifier of trace gases even though in some cases it is not detected in PTR-MS. It is the intended detection  $m/z$  in PTR-MS, and the difference between protonated ion mass and detection  $m/z$  allows fragmentation to be studied systematically. Compound name, elemental composition, and CAS number are also included as compound identifiers.
2. Product ion  $m/z$ s: Detection  $m/z$ s and signal fractions on each of these  $m/z$ s were obtained from calibration and/or measurements in which a gas chromatographic pre-separation method was used [51]. In some cases, only the detection  $m/z$  is included in a publication, in which case, the signal fraction is omitted from the library. All detection  $m/z$  in the library are calculated as exact masses and account for the charge state of the ion to facilitate use of the library with high-resolution mass spectrometers. Because isotopic abundances of the elements are well documented, entries in the library are limited to the most abundant monoisotopic mass of each ion. For example, bromoacetone is detected by PTR-MS with no product-ion fragmentation [51], and the library entry lists  $m/z$  137 ( $\text{C}_3\text{H}_5\text{BrOH}^+$ ) as the only detected  $m/z$  with an intensity of 100%, corresponding to a monoisotopic composition of  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{79}\text{Br}$ , and  $^{16}\text{O}$ . For the library entries where  $[\text{M}+\text{H}_3\text{O}]^+$  is a reported detection  $m/z$ , we make no attempt to discern the mechanism by which the association with  $\text{H}_2\text{O}$  occurred.
3. Instrument details and reference: The electric field strength divided by the number density of the gas inside the reactor ( $E/N$ ) determines the collision energy of ions in the reactor and therefore the degree of fragmentation and cluster formation. We include  $E/N$ , instrument type, and reactor pressure for library entries. Instrument calibration factors are presented in units of normalized counts per second per ppb ( $\text{ncps ppbv}^{-1}$ ), where the signal of the protonated trace gas has been normalized per million counts of  $\text{H}_3\text{O}^+$  reagent ion. While the settings of electrostatic lenses can affect product-ion fragmentation and the flow of water vapor can impact water cluster formation, these parameters are not well documented and are not included in the library. The composition of drift gas in SIFT-MS measurements is included under the “Comments” column. The publication used to construct each entry is listed under the “Reference” column, with links to the publication included in the “doi” column. We envision the library as a tool for researchers to find the original publications, and our hope is that researchers will continue to cite the publications found through the library.
4. Physical molecular properties: Polarizabilities and dipole moments were taken from the *CRC Handbook of Chemistry and Physics* where available [59], and otherwise from the reference listed in the library. Proton affinities are taken from a series of reviews [60]. When reported, measured proton-transfer reaction rate coefficients are included in the library, and we have also followed the procedure of Sekimoto et al., which is based on that of Su, to estimate proton-transfer reaction rate coefficients from each compound's polarizability and dipole moment [10, 61].
5. Chemical molecular properties: SMILES strings and number of functional groups are included in anticipation of studies by linear regression or machine learning to predict sensitivity and product-ion fragmentation patterns from the dataset.

No attempt was made to synthesize information about the same VOC from different studies, with each study contributing a separate library entry for a given compound. Similarly, entries with incomplete information were also included. Our philosophy is that the combined information can serve as a dataset for further analysis, and any attempts to combine multiple studies of a single compound into a single library entry would only reduce the amount of information available.

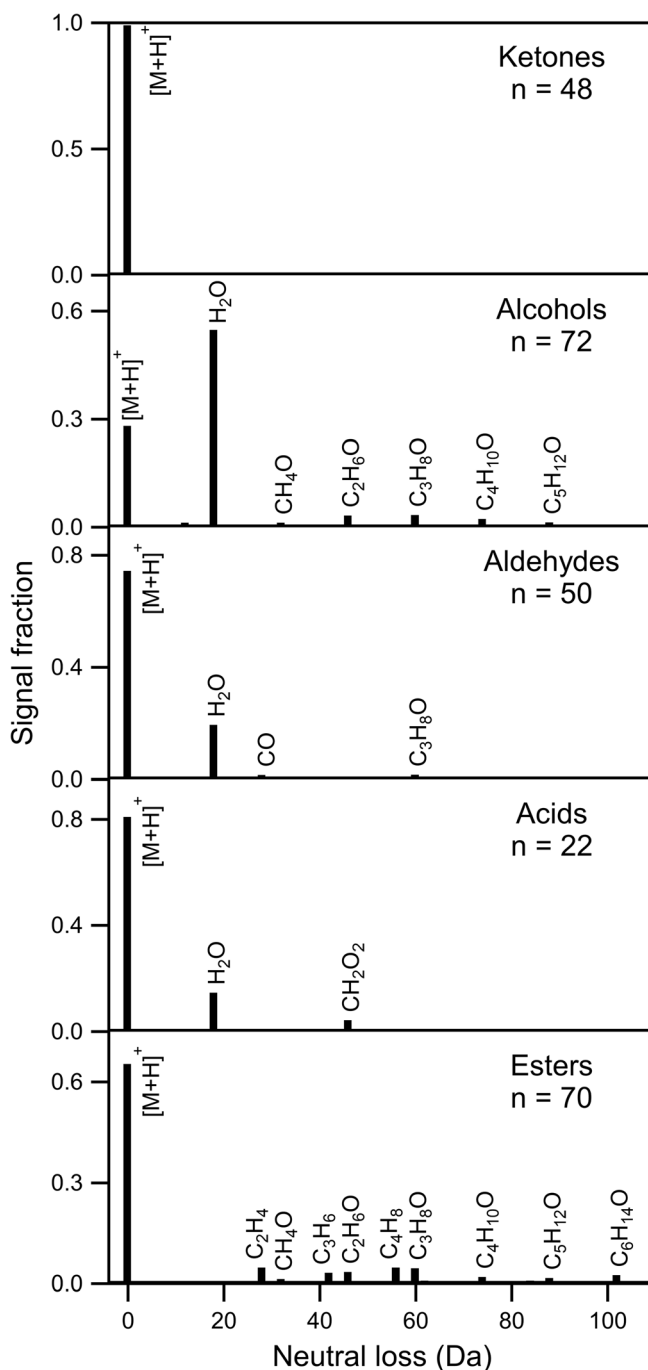
## Product-Ion Fragmentation

A summary of product ion fragmentation is presented in Fig. 1. While the majority of the detected  $m/z$ s are at the parent  $m/z$   $[M+H]^+$  expected from proton transfer reactions, there are many detected fragments. As illustrated by the lines in Fig. 1, the library demonstrates that there are both common fragmentation patterns, such as neutral loss of water and common detected ions, such as  $C_2H_3O^+$ . The library also facilitates systematic exploration of fragmentation patterns of compounds with different functional groups, as demonstrated for oxygenated organic compounds in Fig. 2. The ketones included in the library show virtually no fragmentation, alcohols and aldehydes exhibit neutral loss of water and alcohols, acids lose water and formic acid, and esters lose both alkenes and alcohols.

To summarize the effect product-ion fragmentation can have on bulk properties of a PTR-MS spectrum, we have created histograms of the carbon number, O:C ratio, H:C ratio, and number of ring plus double bond equivalents (DBE) for the compounds in the PTR library and for the product ions at which those compounds are detected. These results are presented in Fig. 3. If no product-ion fragmentation occurred in PTR-MS, the bulk properties of the parent compounds and the product ions would be identical. For entries in the library, product-ion fragmentation decreases the average carbon number from 6.27 to 5.62, decreases the O:C ratio from 0.181 to 0.162, decreases the H:C ratio from 1.86 to 1.76, and increases the average DBE from 1.85 to 2.03. One proton from each product ion was assumed to be the result of the proton transfer reaction, and

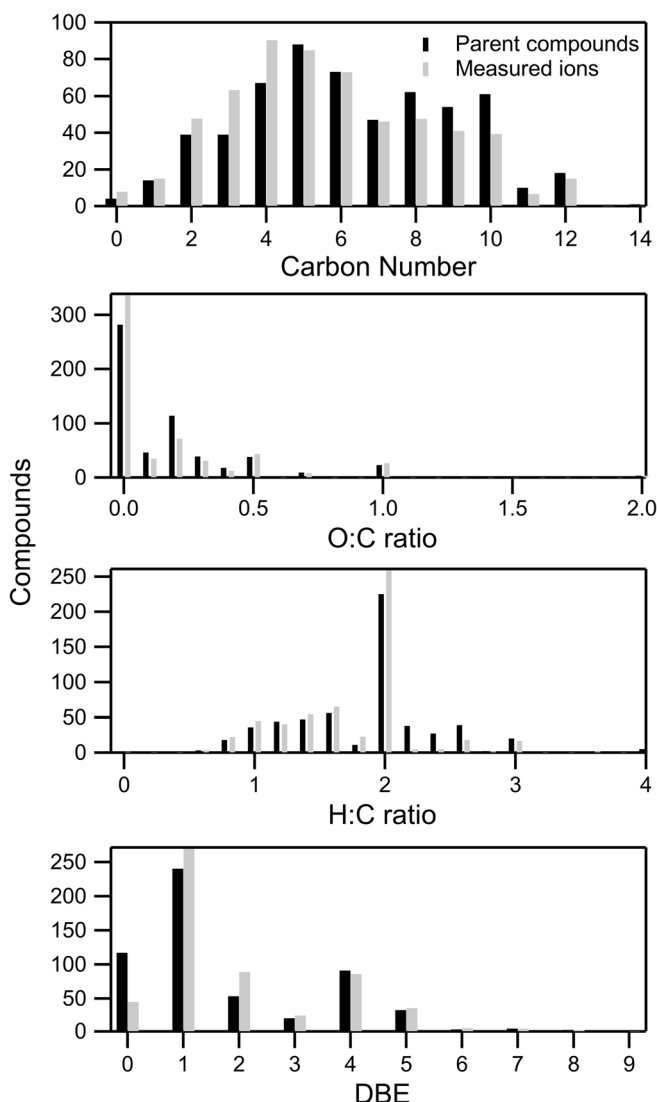


**Figure 1.** Detected ion  $m/z$ s for each parent compound in the PTR library, shaded by relative contribution to total signal. The most abundant ions are shaded black. Patterns emerge for common neutral losses as lines with slope of 1 and for common detected fragments as horizontal lines. A selection of these fragmentation patterns are labeled



**Figure 2.** Neutral losses for oxygenates included in the PTR library for different functional groups, presented as the fraction of total signal detected at each neutral loss for all compounds in the library with the given functional group

that proton is excluded from the calculations of H:C and DBE. In general, product-ion fragmentation involves carbon loss, oxygen loss, and an increase in the extent of unsaturation of an ion. This is consistent with the many observations in the library of oxygenates undergoing neutral loss of water or saturated alcohols, and researchers should account for these losses when relating the bulk properties of a PTR-MS spectrum to a VOC sample. While the results presented in Figs. 1–3 are



**Figure 3.** Histograms comparing the bulk properties of parent compounds in the PTR library to the product ions of those compounds. Product-ion fragmentation documented in the PTR library leads to a decrease in average carbon number, O:C ratio, and H:C ratio and an increase in average ring plus double bond equivalents (DBE)

broad, general observations about product-ion fragmentation, our hope, is that this library will enable more systematic studies of this process and other aspects of proton transfer reactions and that libraries of additional reagent ion chemistries will be developed in the future.

## References

- Lindinger, W., Hansel, A., Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) - medical applications, food control and environmental research. *Int. J. Mass Spectrom. Ion Process.* **173**, 191–241 (1998)
- Smith, D., Španěl, P.: Selected ion flow tube mass spectrometry (SIFT-MS) for on-line trace gas analysis. *Mass Spectrom. Rev.* **24**, 661–700 (2005)
- de Gouw, J., Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrom. Rev.* **26**, 223–257 (2007)
- Yuan, B., Koss, A.R., Warneke, C., Coggon, M., Sekimoto, K., De Gouw, J.A.: Proton-transfer-reaction mass spectrometry: applications in atmospheric sciences. *Chem. Rev.* **117**, 13187–13229 (2017)
- Sulzer, P., Hartungen, E., Hanel, G., Feil, S., Winkler, K., Mutschlechner, P., Haidacher, S., Schottkowsky, R., Gansch, D., Seehauser, H., Striednig, M., Jürschik, S., Breiev, K., Lanza, M., Herbig, J., Märk, L., Märk, T.D., Jordan, A.: A proton transfer reaction-quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF): high speed due to extreme sensitivity. *Int. J. Mass Spectrom.* **368**, 1–5 (2014)
- Yuan, B., Koss, A., Warneke, C., Gilman, J.B., Lerner, B.M., Stark, H., De Gouw, J.A.: A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions ( $\text{H}_3\text{O}^+$  ToF-CIMS) for measurements of volatile organic compounds in the atmosphere. *Atmos. Meas. Tech.* **9**, 2735–2752 (2016)
- Breitenlechner, M., Fischer, L., Hainer, M., Heinritzi, M., Curtius, J., Hansel, A.: PTR3: an instrument for studying the lifecycle of reactive organic carbon in the atmosphere. *Anal. Chem.* **89**, 5824–5831 (2017)
- Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoerner, C., Deming, B., Kimmel, J., Warneke, C., Holzinger, R., Jayne, J., Worsnop, D., Fuhrer, K., Gonin, M., de Gouw, J.: Evaluation of a new reagent-ion source and focusing ion–molecule reactor for use in proton-transfer-reaction mass spectrometry. *Anal. Chem.* **90**, 12011–12018 (2018)
- Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P.M., Soukoulis, C., Aprea, E., Märk, T.D., Gasperi, F., Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry. *Environ. Sci. Technol.* **46**, 2283–2290 (2012)
- Sekimoto, K., Li, S.M., Yuan, B., Koss, A., Coggon, M., Warneke, C., de Gouw, J.: Calculation of the sensitivity of proton-transfer-reaction mass spectrometry (PTR-MS) for organic trace gases using molecular properties. *Int. J. Mass Spectrom.* **421**, 71–94 (2017)
- Dunne, E., Galbally, I.E., Cheng, M., Selleck, P., Molloy, S.B., Lawson, S.J.: Comparison of VOC measurements made by PTR-MS, adsorbent tubes–GC-FID-MS and DNPH derivatization–HPLC during the Sydney particle study, 2012: a contribution to the assessment of uncertainty in routine atmospheric VOC measurements. *Atmos. Meas. Tech.* **11**, 141–159 (2018)
- Gueneron, M., Erickson, M.H., Vanderschelden, G.S., Jobson, B.T.: PTR-MS fragmentation patterns of gasoline hydrocarbons. *Int. J. Mass Spectrom.* **379**, 97–109 (2015)
- Haase, K.B., Keene, W.C., Pszenny, A.A.P., Mayne, H.R., Talbot, R.W., Sive, B.C.: Calibration and intercomparison of acetic acid measurements using proton-transfer-reaction mass spectrometry (PTR-MS). *Atmos. Meas. Tech.* **5**, 2739–2750 (2012)
- Hu, L., Millet, D.B., Kim, S.Y., Wells, K.C., Griffis, T.J., Fischer, E.V., Helmig, D., Hueber, J., Curtis, A.J.: North American acetone sources determined from tall tower measurements and inverse modeling. *Atmos. Chem. Phys.* **13**, 3379–3392 (2013)
- Inomata, S., Tanimoto, H., Kato, S., Suthawaree, J., Kanaya, Y., Pochanart, P., Liu, Y., Wang, Z.: PTR-MS measurements of non-methane volatile organic compounds during an intensive field campaign at the summit of mount tai, China, in June 2006. *Atmos. Chem. Phys.* **10**, 7085–7099 (2010)
- Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., Wang, Z.: Technical note : determination of formaldehyde mixing ratios in air with PTR-MS : laboratory experiments and field measurements. *Atmos. Chem. Phys.* **8**, 273–284 (2008)
- Kajos, M.K., Rantala, P., Hill, M., Hellén, H., Aalto, J., Patokoski, J., Taipale, R., Hoerger, C.C., Reimann, S., Ruuskanen, T.M., Rinne, J., Petäjä, T.: Ambient measurements of aromatic and oxidized VOCs by PTR-MS and GC-MS: intercomparison between four instruments in a boreal forest in Finland. *Atmos. Meas. Tech.* **8**, 4453–4473 (2015)
- Karl, T.G., Christian, T.J., Yokelson, R.J., Artaxo, P., Hao, W.M., Guenther, A.: The tropical forest and fire emissions experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR, and GC from tropical biomass burning. *Atmos. Chem. Phys.* **7**, 5883–5897 (2007)

19. Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdinger-Blatt, I.S., DiGangi, J.P., Sive, B., Turnipseed, A., Hombrook, R.S., Zheng, W., Flocke, F.M., Guenther, A., Keutsch, F.N., Apel, E., Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest. *Atmos. Chem. Phys.* **13**, 2893–2906 (2013)
20. Koss, A.R., Sekimoto, K., Gilman, J.B., Selimovic, V., Coggon, M.M., Zarzana, K.J., Yuan, B., Lerner, B.M., Brown, S.S., Jimenez, J.L., Krechmer, J., Roberts, J.M., Warneke, C., Yokelson, R.J., de Gouw, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment. *Atmos. Chem. Phys.* **18**, 3299–3319 (2018)
21. Ammann, C., Spirig, C., Neftel, A., Steinbacher, M., Komenda, M., Schaub, A.: Application of PTR-MS for measurements of biogenic VOC in a deciduous forest. *Int. J. Mass Spectrom.* **239**, 87–101 (2004)
22. Ma, Y., Diaio, Y., Zhang, B., Wang, W., Ren, X., Yang, D., Wang, M., Shi, X., Zheng, J.: Detection of formaldehyde emissions from an industrial zone in the Yangtze River Delta region of China using a proton transfer reaction ion-drift chemical ionization mass spectrometer. *Atmos. Meas. Tech.* **9**, 6101–6116 (2016)
23. Smith, D., Chippendale, T.W.E., Spanel, P.: Selected ion flow tube, SIFT, studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with some biologically active isobaric compounds in preparation for SIFT-MS analyses. *Int. J. Mass Spectrom.* **303**, 81–89 (2011)
24. Smith, D., Sovová, K., Spanel, P.: A selected ion flow tube study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with seven isomers of hexanol in support of SIFT-MS. *Int. J. Mass Spectrom.* **319–320**, 25–30 (2012)
25. Smith, D., Wang, T., Spanel, P.: Analysis of ketones by selected ion flow tube mass spectrometry. *Rapid Commun. Mass Spectrom.* **17**, 2655–2660 (2003)
26. Sovová, K., Dryahina, K., Spanel, P.: Selected ion flow tube (SIFT) studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with six volatile phytochemical esters. *Int. J. Mass Spectrom.* **300**, 31–38 (2011)
27. Spanel, P., Diskin, A.M., Wang, T., Smith, D.: A SIFT study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with hydrogen peroxide and peroxyacetic acid. *Int. J. Mass Spectrom.* **228**, 269–283 (2003)
28. Spanel, P., Van Doren, J.M., Smith, D.: A selected ion flow tube study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with saturated and unsaturated aldehydes and subsequent hydration of the product ions. *Int. J. Mass Spectrom.* **213**, 163–176 (2002)
29. Spanel, P., Ji, Y., Smith, D.: SIFT studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with a series of aldehydes and ketones. *Int. J. Mass Spectrom. Ion Process.* **165–166**, 25–37 (1997)
30. Spanel, P., Pavlik, M., Smith, D.: Reactions of H<sub>3</sub>O<sup>+</sup> and OH-ions with some organic molecules; applications to trace gas analysis in air. *Int. J. Mass Spectrom. Ion Process.* **145**, 177–186 (1995)
31. Spanel, P., Smith, D.: Selected ion flow tube studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with some organosulphur molecules. *Int. J. Mass Spectrom.* **176**, 167–176 (1998)
32. Aprea, E., Biasioli, F., Märk, T.D., Gasperi, F.: PTR-MS study of esters in water and water/ethanol solutions: fragmentation patterns and partition coefficients. *Int. J. Mass Spectrom.* **262**, 114–121 (2007)
33. Spanel, P., Smith, D.: Selected ion flow tube studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with several amines and some other nitrogen-containing molecules. *Int. J. Mass Spectrom.* **176**, 203–211 (1998)
34. Spanel, P., Smith, D.: Selected ion flow tube studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with several aromatic and aliphatic monosubstituted halocarbons. *Int. J. Mass Spectrom.* **189**, 213–223 (1999)
35. Spanel, P., Smith, D.: Selected ion flow tube studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with eleven amine structural isomers of C<sub>5</sub>H<sub>13</sub>N. *Int. J. Mass Spectrom.* **185–187**, 139–147 (1999)
36. Spanel, P., Smith, D.: SIFT studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with a series of volatile carboxylic acids and esters. *Int. J. Mass Spectrom. Ion Process.* **172**, 137–147 (1998)
37. Spanel, P., Smith, D.: SIFT studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with a series of alcohols. *Int. J. Mass Spectrom. Ion Process.* **167–168**, 375–388 (1997)
38. Spanel, P., Smith, D.: Selected ion flow tube studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> with several aromatic and aliphatic hydrocarbons. *Int. J. Mass Spectrom.* **181**, 1–10 (1998)
39. Španěl, P., Wang, T., Smith, D.: A selected ion flow tube, SIFT, study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> ions with a series of diols. *Int. J. Mass Spectrom.* **218**, 227–236 (2002)
40. Sprung, D., Jost, C., Reiner, T., Hansel, A., Wisthaler, A.: Acetone and acetonitrile in the tropical Indian Ocean boundary layer and free troposphere: aircraft-based intercomparison of AP-CIMS and PTR-MS measurements. *J. Geophys. Res. Atmos.* **106**, 28511–28527 (2001)
41. Steinbacher, M., Dommen, J., Ammann, C., Spirig, C., Neftel, A., Prevot, A.S.H.: Performance characteristics of a proton-transfer-reaction mass spectrometer (PTR-MS) derived from laboratory and field measurements. *Int. J. Mass Spectrom.* **239**, 117–128 (2004)
42. Stockwell, C.E., Veres, P.R., Williams, J., Yokelson, R.J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry. *Atmos. Chem. Phys.* **15**, 845–865 (2015)
43. Buhr, K., Van Ruth, S., Delahunty, C.: Analysis of volatile flavour compounds by proton transfer reaction-mass spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds. *Int. J. Mass Spectrom.* **221**, 1–7 (2002)
44. Wang, T., Spanel, P., Smith, D.: Selected ion flow tube, SIFT, studies of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with eleven C<sub>10</sub>H<sub>16</sub> monoterpenes. *Int. J. Mass Spectrom.* **228**, 117–126 (2003)
45. Wang, T., Spanel, P., Smith, D.: A selected ion flow tube study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with some phenols, phenyl alcohols and cyclic carbonyl compounds in support of SIFT-MS and PTR-MS. *Int. J. Mass Spectrom.* **239**, 139–146 (2004)
46. Wang, T., Spanel, P., Smith, D.: A selected ion flow tube, SIFT, study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> ions with several N- and O-containing heterocyclic compounds in support of SIFT-MS. *Int. J. Mass Spectrom.* **237**, 167–174 (2004)
47. Warneke, C., Roberts, J.M., Veres, P., Gilman, J., Kuster, W.C., Burling, I., Yokelson, R., De Gouw, J.A.: VOC identification and intercomparison from laboratory biomass burning using PTR-MS and PIT-MS. *Int. J. Mass Spectrom.* **303**, 6–14 (2011)
48. Warneke, C., Van Der Veen, C., Luxembourg, S., De Gouw, J.A., Kok, A.: Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration, humidity dependence, and field intercomparison. *Int. J. Mass Spectrom.* **207**, 167–182 (2001)
49. Warneke, C., Veres, P., Murphy, S.M., Soltis, J., Field, R.A., Graus, M.G., Koss, A., Li, S.M., Li, R., Yuan, B., Roberts, J.M., De Gouw, J.A.: PTR-QMS versus PTR-TOF comparison in a region with oil and natural gas extraction industry in the Uintah Basin in 2013. *Atmos. Meas. Tech.* **8**, 411–420 (2015)
50. Warneke, C., Veres, P., Holloway, J.S., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F.C., Graus, M., Gilman, J.B., de Gouw, J.A.: Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results. *Atmos. Meas. Tech.* **4**, 2345–2358 (2011)
51. Warneke, C., de Gouw, J.A., Kuster, W.C., Goldan, P.D., Fall, R.: Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic pre-separation method. *Environ. Sci. Technol.* **37**, 2494–2501 (2003)
52. Yáñez-Serrano, A.M., Nölscher, A.C., Williams, J., Wolff, S., Alves, E., Martins, G.A., Bourtsoukidis, E., Brito, J., Jardine, K., Artaxo, P., Kesselmeier, J.: Diel and seasonal changes of biogenic volatile organic compounds within and above an Amazonian rainforest. *Atmos. Chem. Phys.* **15**, 3359–3378 (2015)
53. Stönnner, C., Derstroff, B., Klüpfel, T., Crowley, J.N., Williams, J.: Glyoxal measurement with a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS): characterization and calibration. *J. Mass Spectrom.* **52**, 30–35 (2017)
54. Cui, L., Zhang, Z., Huang, Y., Lee, S.C., Blake, D.R., Ho, K.F., Wang, B., Gao, Y., Wang, X.M., Louie, P.K.K.: Measuring OVOCs and VOCs by PTR-MS in an urban roadside microenvironment of Hong Kong: relative humidity and temperature dependence, and field inter-comparisons. *Atmos. Meas. Tech.* **9**, 5763–5779 (2016)
55. de Gouw, J.A., Goldan, P.D., Warneke, C., Kuster, W.C., Roberts, J.M., Marchewka, M., Bertman, S.B., Pszenny, A.A.P., Keene, W.C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England air quality study (NEAQS) in 2002. *J. Geophys. Res. Atmos.* **108**, 4682–4699 (2003)
56. de Gouw, J.A., Warneke, C., Stohl, A., Wollny, A.G., Brock, C.A., Cooper, O.R., Holloway, J.S., Trainer, M., Fehsenfeld, F.C., Atlas, E.L., Donnelly, S.G., Stroud, V., Lueb, A.: Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada. *J. Geophys. Res. Atmos.* **111**, 1–20 (2006)

57. Diskin, A.M., Wang, T., Smith, D., Spinel, P.: A selected ion flow tube (SIFT), study of the reactions of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> ions with a series of alkenes; in support of SIFT-MS. *Int. J. Mass Spectrom.* **218**, 87–101 (2002)
58. Dryahina, K., Poláček, M., Spinel, P.: A selected ion flow tube, SIFT, study of the ion chemistry of H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> with several nitroalkanes in the presence of water vapour. *Int. J. Mass Spectrom.* **239**, 57–65 (2004)
59. Lide, D.R.: *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton (2005)
60. Hunter, E.P.L., Lias, S.G.: Evaluated gas phase basicities and proton affinities of molecules: an update. *J. Phys. Chem. Ref. Data.* **27**, 413–656 (1998)
61. Su, T.: Parametrization of kinetic energy dependences of ion–polar molecule collision rate constants by trajectory calculations. *J. Chem. Phys.* **100**, 4703–4703 (1994)