# Using Proton Transfer Reaction Mass Spectrometry for Online Analysis of Secondary Organic Aerosols

*Supporting Information*

HEIDI HELLÉN*, JOSEF DOMMEN*, AXEL METZGER, ASTRID GASCHO, JONATHAN DUPLISSY, TORSTEN TRITSCHER, ANDRE S.H. PREVOT, URS BALTENSPERGER

Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

*Corresponding authors. E-mail: heidi.hellen@fmi.fi, josef.dommen@psi.ch

Fax: 0041 56 310 45 25

**Summary**

The following 5 pages contain 4 tables and 1 figure. A table summarizes the input concentrations of the smog chamber experiments. The other tables present the masses having the highest (>0.8%) contribution to total SOA concentration (ppbv) and the partitioning coefficients ($m^3$ $\mu g^{-1}$) of different masses measured with PTR-MS. The figure shows the ratio of total aerosol mass concentrations measured with PTR-MS and SMPS during smog chamber experiments

Table S1. Initial input concentrations for smog chamber experiments (1-7).

| | | VOC (ppbv) | $NO_2$ (ppbv) | NO (ppbv) | $SO_2$ (ppbv) |
|---|---|---|---|---|---|
| 1 | 1,3,5-TMB | 1200 | 300 | 300 | 2 |
| 2 | 1,3,5-TMB | 1200 | 300 | 300 | 5 |
| 3 | 1,3,5-TMB | 1200 | 300 | 300 | 2 |
| 4 | 1,3,5-TMB | 1200 | 300 | 300 | 0 |
| 5 | α-pinene | 240 | 120 | 120 | 2 |
| 6 | α-pinene | 240 | 120 | 120 | 2 |
| 7 | α-pinene | 240 | 120 | 120 | 0 |

Table S2. Mass to charge ratios having the highest (>0.8%) contribution to total SOA concentration (ppbv) measured with PTR-MS. Masses shown comprise 97% and 94% of total measured concentration for 1,3,5-TMB and α-pinene, respectively.

| TMB | | | | α-pinene | | | |
|---|---|---|---|---|---|---|---|
| m/z 43 | 15.0% | m/z 201 | 1.8% | m/z 43 | 9.8% | m/z 139 | 2.0% |
| m/z 113 | 8.0% | m/z 75 | 1.6% | m/z 59 | 5.9% | m/z 167 | 2.0% |
| m/z 61 | 8.0% | m/z 115 | 1.5% | m/z 71 | 3.4% | m/z 153 | 2.0% |
| m/z 73 | 6.5% | m/z 151 | 1.4% | m/z 141 | 3.2% | m/z 151 | 1.9% |
| m/z 97 | 4.7% | m/z 167 | 1.3% | m/z 127 | 3.0% | m/z 155 | 1.8% |
| m/z 111 | 4.6% | m/z 199 | 1.2% | m/z 125 | 2.9% | m/z 183 | 1.7% |
| m/z 87 | 3.9% | m/z 157 | 1.1% | m/z 97 | 2.9% | m/z 169 | 1.6% |
| m/z 125 | 3.1% | m/z 153 | 1.0% | m/z 69 | 2.8% | m/z 123 | 1.6% |
| m/z 45 | 3.1% | m/z 117 | 1.0% | m/z 107 | 2.8% | m/z 199 | 1.4% |
| m/z 129 | 2.9% | m/z 103 | 0.9% | m/z 61 | 2.7% | m/z 157 | 1.4% |
| m/z 139 | 2.6% | | | m/z 113 | 2.6% | m/z 73 | 1.4% |
| m/z 59 | 2.5% | | | m/z 115 | 2.6% | m/z 181 | 1.3% |
| m/z 99 | 2.4% | | | m/z 99 | 2.6% | m/z 101 | 1.3% |
| m/z 109 | 2.3% | | | m/z 85 | 2.3% | m/z 129 | 1.2% |
| m/z 127 | 2.2% | | | m/z 87 | 2.3% | m/z 171 | 1.2% |
| m/z 123 | 2.1% | | | m/z 47 | 2.2% | m/z 165 | 1.1% |
| m/z 185 | 2.1% | | | m/z 81 | 2.2% | m/z 185 | 1.0% |
| m/z 101 | 2.0% | | | m/z 95 | 2.1% | m/z 93 | 0.9% |
| m/z 169 | 2.0% | | | m/z 111 | 2.1% | m/z 75 | 0.9% |
| m/z 141 | 1.9% | | | m/z 83 | 2.0% | m/z 137 | 0.9% |
| m/z 85 | 1.9% | | | m/z 109 | 2.0% | m/z 201 | 0.8% |

Table S3. Partitioning coefficients ($m^3$ $\mu g^{-1}$) of different masses measured with PTR-MS when the SOA mass was highest during 1,3,5-TMB experiments.

| Experiment | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| SOA mass ($\mu g\ m^{-3}$) | 143 | 219 | 158 | 160 |
| m/z 43 | 1.40E-04 | 1.08E-04 | 1.31E-04 | 9.62E-05 |
| m/z 61 | 6.37E-05 | 6.38E-05 | 8.21E-05 | 4.72E-05 |
| m/z 73 | 5.54E-05 | 4.01E-05 | 5.39E-05 | 2.02E-05 |
| m/z 75 | 2.84E-04 | 1.46E-04 | 2.33E-04 | 1.57E-04 |
| m/z 85 | 3.45E-04 | 1.60E-04 | 3.06E-04 | 5.35E-04 |
| m/z 87 | 1.80E-04 | 1.16E-04 | 1.39E-04 | 1.22E-04 |
| m/z 97 | 9.23E-04 | 6.32E-04 | 9.00E-04 | 9.22E-04 |
| m/z 99 | 4.71E-04 | 2.49E-04 | 4.85E-04 | 9.44E-04 |
| m/z 101 | 1.76E-04 | 1.63E-04 | 2.77E-04 | 2.30E-04 |
| m/z 103 | 8.42E-04 | 5.01E-04 | 6.25E-04 | 4.28E-04 |
| m/z 109 | 6.03E-04 | 2.73E-04 | 3.85E-04 | 6.43E-04 |
| m/z 111 | 1.22E-04 | 7.59E-05 | 1.11E-04 | 1.04E-04 |
| m/z 113 | 1.66E-04 | 8.10E-05 | 1.33E-04 | 1.28E-04 |
| m/z 115 | 2.12E-04 | 1.49E-04 | 1.76E-04 | 1.96E-04 |
| m/z 117 | 4.29E-04 | 3.04E-04 | 3.78E-04 | 2.32E-04 |
| m/z 125 | 9.55E-04 | 1.54E-04 | 3.62E-04 | 2.82E-04 |
| m/z 127 | 5.89E-04 | 3.82E-04 | 4.90E-04 | 5.80E-04 |
| m/z 129 | 5.62E-04 | 3.03E-04 | 3.76E-04 | 6.72E-04 |
| m/z 139 | 2.94E-04 | 1.37E-04 | 1.85E-04 | 1.64E-04 |
| m/z 141 | 3.70E-04 | 1.26E-04 | 1.66E-04 | 1.31E-04 |
| m/z 145 | 5.91E-04 | 4.12E-04 | 5.83E-04 | 6.52E-04 |
| m/z 151 | 6.80E-04 | 3.34E-04 | 4.41E-04 | 8.72E-04 |
| m/z 153 | 8.39E-04 | 5.76E-04 | 1.11E-03 | 1.20E-03 |
| m/z 157 | 7.44E-04 | 2.91E-04 | 4.87E-04 | 5.48E-04 |
| m/z 167 | 3.81E-04 | 3.34E-04 | 4.27E-04 | 4.43E-04 |
| m/z 169 | 1.27E-03 | 5.02E-04 | 7.13E-04 | 1.03E-03 |
| m/z 171 | 8.74E-04 | 5.10E-04 | 6.84E-04 | 5.90E-04 |
| m/z 185 | 7.09E-04 | 4.15E-04 | 9.95E-04 | 5.74E-04 |
| m/z 199 | 8.94E-04 | 7.28E-04 | 9.84E-04 | 1.54E-03 |
| m/z 201 | 8.03E-04 | 5.04E-04 | 6.89E-04 | 6.35E-04 |

Table S4. Partitioning coefficients ($m^3$ $\mu g^{-1}$) of different masses measured with PTR-MS when the SOA mass was highest during α-pinene experiments.

| Experiment | 5 | 6 | 7 |
|---|---|---|---|
| SOA mass (μg $m^{-3}$) | 310 | 302 | 315 |
| m/z 43 | 2.34E-04 | 1.94E-04 | 2.44E-04 |
| m/z 47 | 1.69E-04 | 1.17E-04 | 9.89E-05 |
| m/z 59 | 2.04E-04 | 1.86E-04 | 1.26E-04 |
| m/z 61 | 2.05E-04 | 1.68E-04 | 1.09E-04 |
| m/z 67 | 3.96E-04 | 3.39E-04 | 4.38E-04 |
| m/z 69 | 4.95E-04 | 3.99E-04 | 5.44E-04 |
| m/z 71 | 1.81E-04 | 1.80E-04 | 1.59E-04 |
| m/z 73 | 2.62E-04 | 1.91E-04 | 1.49E-04 |
| m/z 75 | 4.57E-04 | 3.71E-04 | 3.51E-04 |
| m/z 79 | 1.98E-04 | n.a. | 2.35E-04 |
| m/z 83 | 7.13E-04 | 5.09E-04 | 6.82E-04 |
| m/z 85 | 3.96E-04 | 3.99E-04 | 5.45E-04 |
| m/z 87 | 4.07E-04 | 3.45E-04 | 4.25E-04 |
| m/z 89 | 4.67E-04 | 5.41E-04 | 3.39E-04 |
| m/z 93 | 2.69E-04 | 1.64E-04 | 1.76E-04 |
| m/z 95 | 3.77E-04 | 2.65E-04 | 4.37E-04 |
| m/z 97 | 5.28E-04 | 3.44E-04 | 7.12E-04 |
| m/z 99 | 2.72E-04 | 2.32E-04 | 2.87E-04 |
| m/z 101 | 3.08E-04 | 2.83E-04 | 4.64E-04 |
| m/z 103 | 5.42E-04 | 3.31E-04 | 8.72E-04 |
| m/z 107 | 1.56E-04 | 1.29E-04 | 1.87E-04 |
| m/z 109 | 2.69E-04 | 1.59E-04 | 2.47E-04 |
| m/z 111 | 8.92E-04 | 4.59E-04 | 1.54E-03 |
| m/z 113 | 6.47E-04 | 4.85E-04 | 5.72E-04 |
| m/z 115 | 4.18E-04 | 5.38E-04 | 5.87E-04 |
| m/z 121 | 4.85E-04 | 2.50E-04 | 7.05E-04 |
| m/z 123 | 3.35E-04 | 2.60E-04 | 4.30E-04 |
| m/z 125 | 5.39E-04 | 3.65E-04 | 7.60E-04 |
| m/z 127 | 7.61E-04 | 5.26E-04 | 1.40E-03 |
| m/z 129 | 5.51E-04 | 3.44E-04 | 9.25E-04 |
| m/z 135 | 1.63E-04 | 1.08E-04 | 1.61E-04 |
| m/z 139 | 6.85E-04 | 3.86E-04 | 5.85E-04 |
| m/z 141 | 7.29E-04 | 4.96E-04 | 9.52E-04 |
| m/z 143 | 6.24E-04 | 6.77E-04 | 8.77E-04 |
| m/z 145 | 5.84E-04 | 6.13E-04 | 7.88E-04 |
| m/z 151 | 1.07E-04 | 8.32E-05 | 9.32E-05 |
| m/z 153 | 5.90E-04 | 4.14E-04 | 5.78E-04 |
| m/z 155 | 9.40E-04 | 6.62E-04 | 9.22E-04 |
| m/z 157 | 9.98E-04 | 8.44E-04 | 1.29E-03 |
| m/z 165 | 2.30E-03 | 1.49E-03 | 1.81E-03 |
| m/z 167 | 4.70E-04 | 4.44E-04 | 6.25E-04 |
| m/z 169 | 5.16E-04 | 3.20E-04 | 6.29E-04 |
| m/z 171 | 9.98E-04 | 9.63E-04 | 1.33E-03 |
| m/z 181 | 5.35E-03 | 2.04E-03 | 5.89E-03 |
| m/z 183 | 9.30E-04 | 1.32E-03 | 3.44E-03 |
| m/z 185 | 1.49E-03 | 8.08E-04 | 9.84E-04 |
| m/z 197 | 2.71E-03 | 3.13E-03 | 5.30E-03 |
| m/z 199 | 1.88E-03 | 2.95E-03 | 5.76E-03 |
| m/z 201 | 2.90E-03 | 1.63E-03 | 4.40E-03 |

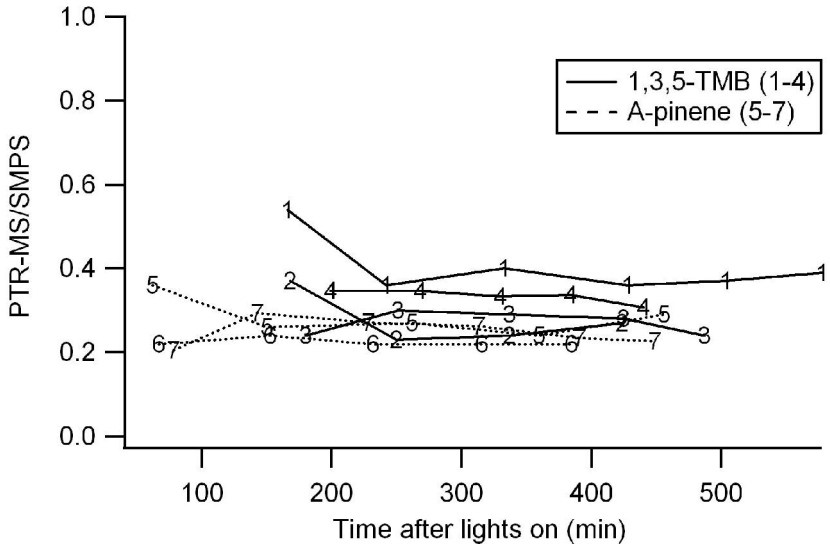


Figure S1. Ratio of total aerosol mass concentrations measured with PTR-MS and SMPS during smog chamber experiments. Densities of 1.4 g $cm^{-3}$ and 1.3 g $cm^{-3}$ were assumed for the aerosols measured with SMPS in TMB and α-pinene experiments, respectively.