Supplement of

ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO-GAW and EMEP observation networks

C. C. Hoerger et al.

Correspondence to: C. C. Hoerger (corinne.hoerger@empa.ch)

42   In the following the set-up and the measurement results of the PTR-MS are presented.

43

PTR-MS instrumentation

45   The proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria) is

46   described in detail by Lindinger et al. (1998), de Gouw et al. (2003), Warneke et al. (2003), de Gouw

47   and Warneke (2007) and the used instrument calibration and data processing method by Taipale et al.

48   (2008). In brief, the air samples are directly fed to the PTR-MS (Ionicon Analytik GmbH, Austria,

49   Table 4) without any drying or other pretreatments. The volatile organic compounds (VOCs) are

50   ionized in a proton transfer reaction with hydronium ions (H_3O^+). The PTR-MS consists of three parts:

51   a discharge ion source to produce the primary ions, a drift-tube reactor, and a quadrupole mass

52   spectrometer for detecting primary and product ions. The H_3O^+ ions are produced in a hollow

53   discharge cathode from pure water vapor and guided to the reaction chamber through a small orifice.

54   The air sample is fed continuously through the drift tube, where the VOCs of the air sample collide

55   with the H_3O^+ ions. If the proton affinity of the VOCs is higher than that one of water, the VOCs are

56   ionized. The H_3O^+ ion performs a non-dissociative proton transfer to a majority of the VOCs. The

57   mole fractions of a target compound were determined from the signal intensity at a specific mass to

58   charge ratio (m/z). Fragmentation or charge transfer from O_2^+ ion was not taken into account. After the

59   drift tube, the ions are guided to a quadrupole mass spectrometer for the selection and detection of the

60   ions. The instrument measures with one Thomson (Th) resolution, thus different compounds with

61   same nominal m/z cannot be distinguished.

62   The instrument of SMR II was calibrated using a VOC calibration standard (Apel-Riemer

63   Environment Inc., Table 4) and VOC free air generated from ambient air with a catalytic converter.

64   The calibration standard was diluted to a mole fraction of a few tens of nmol/mol. The instrumental

65   background of the PTR-MS was determined by measuring VOC free air, and the background signals

66   were subtracted from the measured signals. In the WCC-VOC the PTR-MS was calibrated using three

67   dry gas standards in the low nmol/mol range (D64 1904: 28 hydrocarbon species with amount

68   fractions of about 1 nmol/mol; D64 1977: 17 component monoterpene mixture with benzene, toluene

69   and isoprene, amount fractions about 2 nmol/mol; D838784R: 29 NMHC mixture, amount fractions

70   about 4 nmol/mol; balance gas: nitrogen; National Physical Laboratory (NPL), UK, Central

71   Calibration Laboratory for Non-Methane Hydrocarbons of WMO-GAW).

72

Results and discussion

74   SMEAR II (SMR II), Hyytiälä (Finland), and WCC-VOC, Garmisch-Partenkirchen (Germany)

75   (Figure 1, main paper), reported mole fractions for m/z 69 (parent ion for isoprene), m/z 79 (parent ion

76   for benzene), and m/z 93 (parent ion for toluene and p-cymene) (Figure S1). For the NMHC_N_2 m/z

77   69, WCC-VOC reported an amount fraction well within the ACTRIS data quality objective for

78   isoprene (DQOs, Table 2, main paper), whereas for the NMHC_air a strong overestimation was

79 observed. SMEAR II did not report isoprene. For m/z 93 and m/z 79 the results for both mixtures and
80 for both stations were outside ACTRIS and GAW DQOs for toluene and benzene, respectively.
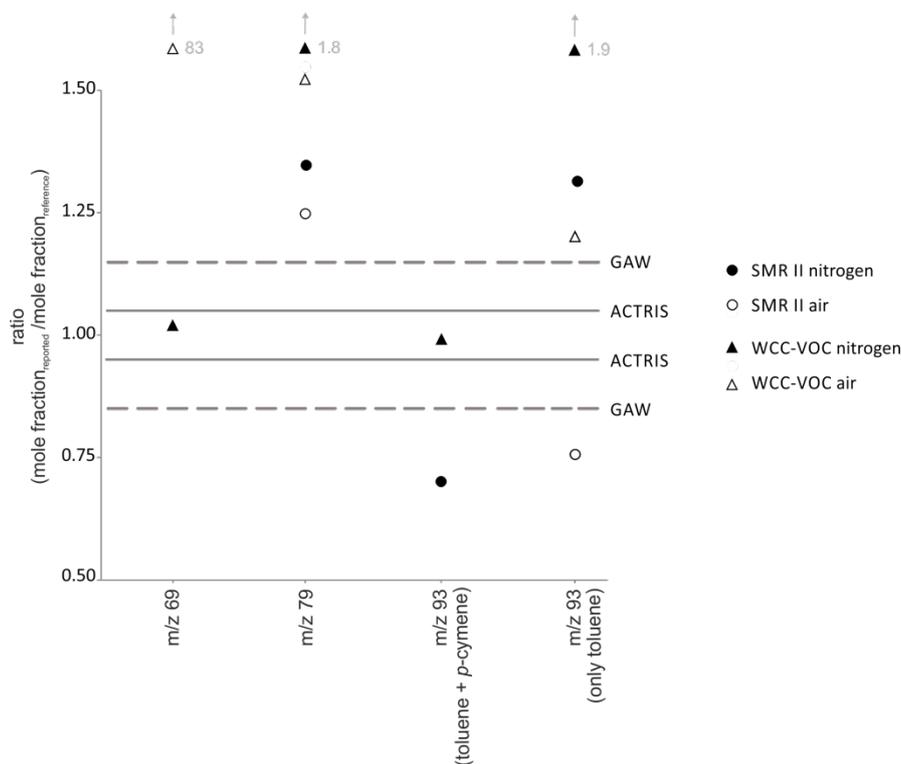
81
82
83 Figure S1: PTR-MS results for m/z 69 (isoprene), m/z 79 (benzene), m/z 93 (toluene + *p*-cymene) and
84 toluene from SMR II and WCC-VOC are presented relative to the reference values. Closed and open
85 circles/triangles indicate results in NMHC_N_2 and NMHC_air, respectively. Solid and dashed grey
86 lines indicate ACTRIS and GAW data quality objectives, respectively (Table 2, main paper).
87

88 The differences to the assigned values in two NMHC mixtures (NMHC_N_2 and NMHC_air) may be
89 attributed to the lack of compound specificity of the PTR-MS analytical system (Blake et al., 2009). It
90 is well known in mass spectroscopy that a detected m/z may be a result of different ions (parent ions,
91 clusters, fragments). In the NMHC_N_2 sample m/z 69 seem to represent isoprene as assigned and
92 measured values are very close as shown by WCC-VOC. In NMHC_air, however, m/z 69 is most
93 likely a mixture of different ions.
94 An ion screening of the NMHC_air by PTR-MS analysis spanning a m/z range from 21 to 161
95 performed by WCC-VOC revealed a huge amount of oxygenated VOC present in the gas cylinder.
96 Compared to back ground air, amount fraction m/z 59 (e.g. parent ion for acetone or propanal) was
97 doubled, m/z 33 (parent ion for methanol) was higher by a factor of 4.5, m/z 45 (e.g. parent ion for
98 acetaldehyde) was increased by a factor of about 10. Amount fractions of other oxygenated VOC with
99 m/z 43 (e.g. parent ion for propanol) and m/z 61 (e.g. parent ion for acetic acid) were 60 times and 200
100 times higher, respectively, as in background air. It is very likely that also for m/z 69 other compounds
101 (e.g. pentanal) as isoprene were co-detected and thus the reported value was the amount fraction of

102 alcohols or aldehydes rather than isoprene. In further GC-MS studies the exact composition of

103 oxygenated VOC present in the ACTRIS air standards should be elucidated.

104 For m/z 79 (benzene) the difference to the assigned values may also be explained by co-detection of

105 compounds. For m/z 93 (toluene + *p*-cymene) WCC-VOC obviously overestimated the toluene target

106 values. As *p*-cymene was present in both gas cylinders this was expected. For NMHC_N_2 the *p*-

107 cymene value was known (1.07 $\pm$ 0.079 nmol/mol). As in m/z 93 both toluene and *p*-cymene were

108 detected, the target mole fraction in NMHC_N_2 for m/z 93 was therefore 2.29 nmol/mol. This target

109 mole fraction of m/z 93 was almost perfectly matched by WCC-VOC with a measured value of 2.27

110 nmol/mol. This highlights the weakness of the PTR-MS method; it does not detect changes in the

111 chemical composition of the gas sample. Thus the PTR-MS was a method for monitoring changes in

112 the concentrations of a known matrix, but not for the identification of the compounds. The reported

113 value for m/z 93 from SMR-II when referenced to the sum of toluene and *p*-cymene in NHMC_N_2

114 underestimated the target by about 30%. The same bias is observed when comparing the SMR-II data

115 for other m/z and other samples to values reported by WCC-VOC. These results may likely be traced

116 back to uncertainties in the calibration process and changes in the gas sample composition.

117 When applying calibration factors for specific compounds gained for dry gas samples to ambient

118 measurement conditions it has to be considered that humidity in the gas sample may influence the

119 instrument response. As some water gets from the ion source to the reaction chamber, as well as from

120 the sample air, water clusters $H_3O^+(H_2O)$ are always present in the reaction chamber. The drift tube

121 ion chemistry includes ionization of the measured compounds as well as formation of water clusters,

122 which are ionized, too. Since there is also some back drift of sample air into the ion source, the

123 abundance of primary ions is also influenced by the air sample, e.g. amount of water vapor (Tani et al.,

124 2003) and oxygen (Ennis et al., 2005). Many compounds have high enough water affinity to be

125 protonated in the collision with the water cluster as well as with protonated water. Additionally,

126 changes in relative humidity do affect the measured signals. However benzene and toluene do not

127 react with water cluster and thus their signals are humidity dependent. The highest signals for benzene

128 and toluene have been measured when the relative humidity was low (20%) and the signals were

129 decreasing with decreasing relative humidity (Warneke et al., 2001).

130 To conclude: while PTR-MS is a real-time, on-line method that is less labor intense than the GC-MS

131 methods for monitoring changes in mole fractions, another method is needed for determining the

132 chemical composition of the gas samples. For correctly assigning amount fractions with PTR-MS

133 analysis to specific compounds, the composition of the gas matrix needs to be considered as well as

134 cluster formation and compound fragmentation. In addition, standards used for calibration should be

135 traceable to a common scale and if diluted standards are used, the error in the dilution ratio must be as

136 small as possible to minimize the bias to target amount fractions.

137

138 **<u>References</u>**

139 Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chem.
140 Rev., 109, 861–896, 2009.

141

142 De Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere
143 using proton-transfer-reaction mass spectrometry, Mass Spectrom Rev, 26, 223-257, 2007.

144

145 De Gouw, J., Warneke, C., Karl, T., Eerdekens, G., Van der Veen, C., and Fall, R.: Sensitivity and
146 specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J.
147 Mass Spectrom., 223-224, 365-382, 2003a.

148

149 de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman,
150 S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry
151 (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England
152 Air Quality Study (NEAQS) in 2002, Journal of Geophysical Research D: Atmospheres, 108, ACH
153 10-11 - ACH 10-18, 2003b.

154

155 Ennis, C. J., Reynolds, J. C., Keely, B. J., and Carpenter, L. J.: A hollow cathode proton transfer
156 reaction time of flight mass spectrometer, Int. J. Mass Spectrom., 247, 72-80, 2005.

157

158 Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv
159 levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications,
160 food control and environmental research, Int. J. Mass Spectrom. Ion Proces., 173, 191-241, 1998.

161

162 Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.:
163 Technical note: Quantitative long-term measurements of VOC concentrations by PTR-MS -
164 Measurement, calibration, and volume mixing ratio calculation methods, Atmospheric Chemistry and
165 Physics, 8, 6681-6698, 2008.

166

167 Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by
168 proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223-224, 561-578,
169 2003.

170

171 Warneke, C., De Gouw, J. A., Kuster, W. C., Goldan, P. D., and Fall, R.: Validation of atmospheric
172 VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic
173 preseparation method, Environmental Science and Technology, 37, 2494-2501, 2003.

174

175 Warneke, C., Van Der Veen, C., Luxembourg, S., De Gouw, J. A., and Kok, A.: Measurements of
176 benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: Calibration,
177 humidity dependence, and field intercomparison, Int. J. Mass Spectrom., 207, 167-182, 2001.

178
179