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Atmospheric Measurement Techniques Discussions

Interactive comment on "Potential of needle trap microextraction – portable gas chromatography – mass spectrometry for measurement of atmospheric volatile compounds" *by* Luís Miguel Feijó Barreira et al.

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Answers to reviewer's comments

(1) Authors should consider addition of more references to the NTME technique. Apart from environmental analysis, there are several interesting articles about NTME dealing with optimization of adsorption and desorption parameters affecting the efficient preconcentration of volatile organic compound. In this regard, authors may consider the following additions/clarifications: - Introduction, p. 2, line 34: after the sentence ": : : of the sorbent packed in the needle (Eom et al., 2008)." add the information

that - additionally to the mentioned volume of adsorbent - also the type of adsorbent material (microporosus/mesoporous structure, mechanical/thermal stability) as well as sampling parameters (temperature and sample flow rate during adsorption) affect the reproducibility and efficiency of adsorptive preconcentration on needle trap devices as demonstrated by Filipiak et al. [doi:10.1088/1752-7155/6/2/027107 J. Breath Res. 6 (2012) 027107]. Furthermore, the robustness, easiness and rapidity of the analysis with NTME were shown to be superior for the BTEX determination in gaseous and even in aqueous samples [Jurdakova et al., doi:10.1016/j.chroma.2008.04.065 J. Chrom. A, 1194, 2008, 161–164].

(2) The references were added to the manuscript.

(3) Page 3, line 3: It was demonstrated that NTME was easy, fast and robust in a study on determination of trace amounts of BTEX in water by GC-FID (Jurdáková et al., 2008). The type of adsorbent material (microporous/mesoporous, mechanical/thermal stability) and sampling parameters (such as temperature and sample flow during adsorption) affect the efficiency and reproducibility of adsorption on needle trap devices (Filipiak et al., 2012).

(1) Section 2.3, p. 3, line 30: it would be helpful to explain to a reader what exactly is "CUSTODION® needle trap microextraction syringe", as there is no information about this device on a manufacturer's website (http://torion.com/products/custodion.html). It is particularly interesting exactly how was a thermal desorption performed, as authors mention "syringe" in terms of needle trap device (NTD), whereas desorption from needle traps is typically done by simple insertion of NTD (plugged on other end) into GC injector (operating at preset temperature): : : Did authors use additional sample-flow through the needle trap during injection to GC?

(2) Manufacturer′s reference on NTD can be found at http://torion.com/fileadmin/media/documents/applications/TLPN_1245_Torion_Application_E Thermal desorption was performed by inserting the needle trap device into the in-

jection port of the GC-MS (at 270 °C). External flow of carrier gas was not needed. A more detailed description about the thermal desorption process was added to the manuscript.

(3) Page 5, line 7: The injector assembly allows for a proper flow of carrier gas through the side-hole placed above the adsorbent material in the needle trap, which directs the desorbed compounds into the GC column during thermal desorption.

(1) Section 2.3, p. 4, line 8: authors used 25 ml/min sample flow rate over 100 minutes for adsorption on Needle Trap Device (NTD), what results in 2,5 L of sample drag through needle trap. Are the authors sure that there is no saturation of adsorbents in needle trap? This is very large volume of sample, typically used for adsorption on conventional "sorption tubes" (sampling tubes) filled with incomparably larger amounts of the same adsorbents. . .

(2) An additional study on the needle trap breakthrough volume was added to the manuscript. No saturation was observed for a concentration of 386 ppbV of α-pinene, which is significantly higher than ones usually observed for monoterpenes, aromatics and carbonyl compounds in Hyytiälä ambient air (eg. Hellén et al., 2004). (3) Page 4, line 24: To ensure sufficient capacity of the sampler and that the breakthrough volume is not reached during sampling of 2.5 L of air, following study was performed. One μL of α-pinene was evaporated by heating in a headspace vial (20 mL), from which 0.5 mL of gas phase was transferred by gas-tight syringe to a Teflon bag (Tedlar®, 10 L, Sigma Aldrich) filled with nitrogen. The final concentration was 386 ppbV, which is significantly higher than the concentrations usually measured in the ambient air (e.g. Hellén et al., 2004). A sampling kit (Pas Technology, Germany) was used for collection of different volumes of α-pinene from the Tedlar bag into the needle trap device, and samples were analyzed by GC-MS. As can be seen in Fig. S2, a good linearity was observed for all volumes sampled, which strongly suggest that saturation or breakthrough volume was not achieved during the field measurements. (1) Section 2.3, p. 4, line 23: in extracted ion chromatograms it has no sense to use m/z=83 for propionaldehyde. This compound

has a molecular weight of 58 and simply cannot generate a signal at m/z=83.

(2) The compound is pinonaldehyde (C10H16O2, MW = 168.23 g/mol), an oxidation product of α-pinene.

(3) No changes has been made.

(1) Section 3, p. 4, line 30: if authors state that "factors affecting sensitivity and chromatographic separation including peak shape were considered", they should also provide information which exactly factors were taken into consideration, what is the effect, why certain parameters (what values) were selected etc. In a present form such statement does not bring much information...

(2) Collection time, split ratio and duration were optimized. The choice of collection time was already justified by the trace levels of studied compounds found in the ambient air. The changes on the previous developed method for an increase in sensitivity, without compromising the chromatographic separation, are now described in the manuscript.

(3) Page 5, line 31: Portable gas chromatography-mass spectrometry method employed in this study has been developed for the analysis of VOCs in our previous research (Barreira et al., 2015). The system was further developed in this work by including needle trap microextraction to allow higher sampling capacity of VOCs. In contrast to our previous study, where solid-phase microextraction was used, NTME is more robust and enables exhaustive sampling. Minor modifications on the previous method, such as shorter split time, were performed in order to improve sensitivity without compromising the peak shapes.

(1) Section 3, p. 4, line 32: authors normalized the peak areas to the adsorbed gas volume. This could be done only in case of linear relationship of the acquired peak area and adsorbed sample volume (i.e. no saturation of NTD). Could authors present a proof that collecting 2,5L of sample on needle trap still guarantees this linearity?

(2) The linear relationship between acquired peak area and adsorbed sample volume

was demonstrated in the study on the breakthrough volume, which was added to the manuscript.

(3) Page 4, line 24: To ensure sufficient capacity of the sampler and that the breakthrough volume is not reached during sampling of 2.5 L of air, following study was performed. One μL of α-pinene was evaporated by heating in a headspace vial (20 mL), from which 0.5 mL of gas phase was transferred by gas-tight syringe to a Teflon bag (Tedlar®, 10 L, Sigma Aldrich) filled with nitrogen. The final concentration was 386 ppbV, which is significantly higher than the concentrations usually measured in the ambient air (e.g. Hellén et al., 2004). A sampling kit (Pas Technology, Germany) was used for collection of different volumes of α-pinene from the Tedlar bag into the needle trap device, and samples were analyzed by GC-MS. As can be seen in Fig. S2, a good linearity was observed for all volumes sampled, which strongly suggest that saturation or breakthrough volume was not achieved during the field measurements. (1) 3. Technical Correction Authors are asked to clarify the description of sampling procedure in the following way: If there was no syringe (containing a sample) connected to a needle trap, authors should not use the term “needle trap syringe” (e.g. p.4, line 3) but “needle trap device” or an abbreviation “NTD” thorough the manuscript. b) If there was a syringe (with sample) connected to a needle trap, it should be stated clearer (but this would mean 2,5L syringe, according to author’s description of sampling). Perhaps, authors could add a sketch depicting the system used.

(2) The term “needle trap syringe” was corrected to needle trap device. A sketch depicting the system was added to the manuscript.

(3) Page 4, line 10: Needle trap device was installed in a commercial air sampling interface (Fig. S1) made for needle trap devices (Torion Technologies Inc.).

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Supplemental material for “Potential of needle trap microextraction – portable gas chromatography – mass spectrometry for measurement of atmospheric volatile compounds”

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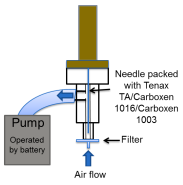

Figure S1: Schematic representation of collection system used for needle trap microextraction device.

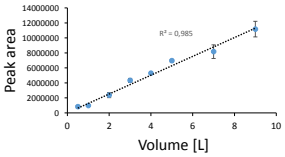

Figure S2: Extraction volume vs peak area of α-pinene obtained by NTME and GC-MS.

Fig. 1.