LTP-MS of PM2.5 filters sampled in dwellings – A new and simple fingerprinting method

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Keywords: Inhalable particles, phthalates, fatty acids, screening

1 Introduction

Inhalable particles ($PM_{2.5}$) is a known risk factor for adverse health effects like cardiovascular diseases and respiratory symptoms. The particle size is not the only factor to determine the health effects. Chemicals adsorbed to the particles might also have an effect.

Five Danish dwellings have been subject to a pilot study throughout an entire year (2010/2011). Seasonal variation of air exchange (Gustavsen et al. 2011), microbiology (Frankel et. al. 2011) and the ratio of different chemicals in airborne dust are investigated.

In the present study $PM_{2.5}$ filters are analyzed directly without sample preparation by use of Low Temperature Plasma Ionization (LTP), a new ambient ionization method for mass spectrometry (MS). This yields a fast method for screening and fingerprinting of the relative abundance of the dominating species as an alternative to extraction followed by HPLC-MS. Further ozone is sampled with passive samplers. Indoor and outdoor average air concentrations over the 4 day sampling campaigns are related to the differences in the fingerprinting.

2 Materials/Methods

Five homes (A-E) in the Copenhagen area were selected among volunteer families. Homes with smoking inhabitants were excluded from the selection. One home was selected because of reported mould problems. The homes can shortly be summarized: Home A is a one-family house with 3 inhabitants and one dog; Home B: An one-family house with two floors and a basement, 4 inhabitants and one cat; home C: A townhouse with 2 inhabitants; home D: An apartment with one inhabitant and home E: An one-family house with a basement and 2 inhabitants.

$PM_{2.5}$ was sampled with a cyclone on Teflon filters at an airflow of 4 L/min. Each filter was sampled for 4 days (Thursday-Monday), giving a total sample volume of app. 23000 L. Four sampling campaigns were performed during the four seasons (May/spring, August/summer, September/October/fall and January/winter). One filter was sampled in the bedroom and another in the living room, giving a total of 40 samples.

The filters were analyzed without further sample preparation with a homebuild LTP ion source as developed by Harper et. al. (2008) coupled to a Bruker microQ-TOF. The LTP was operated at an alternating voltage of 3.3 kHz and He was used as discharge gas at a flow of app 0.4 L/min. For each sample the MS was run in continuous mode. In the beginning of each sample collection, the signal from an unexposed filter was collected as used as background subtraction from the sample. The data from each sample was averaged over app 2 min with sampling at 2-3 different spots on the same filter.

MS spectra were obtained in both positive and negative mode. The fingerprints in LTP-MS will later be compared with Pressurized Liquid Extraction (PLE) of the filters followed by LC-MS analysis.

3 Results

In negative mode the most abundant peaks in the mass spectrum was *m/z* = 199, 227, 241, 255 and 283 as shown in Figure 1. Theses masses correspond well to the homologous series of saturated fatty acids (C12-C18), with *m/z* = 241 as the only ion with an uneven number of carbon atoms (C15). The most dominating peak at *m/z* = 255 (C16) is the saturated form of the monounsaturated fatty acid, sapienic acid, which

is a major component of human sebum (Drake et. al. 2008), and therefore expected to be found in significant amounts in house dust. This indicates that a reduction of the double bond might occur, either during aging in the dust or during the ionization process.

The preliminary results suggest that the presence of a dog in the home has an effect on the composition of the fatty acids found in the house dust. It can be seen as an increase in the peak *m/z* = 283. Such an increase is not seen in the home with feline inhabitants.

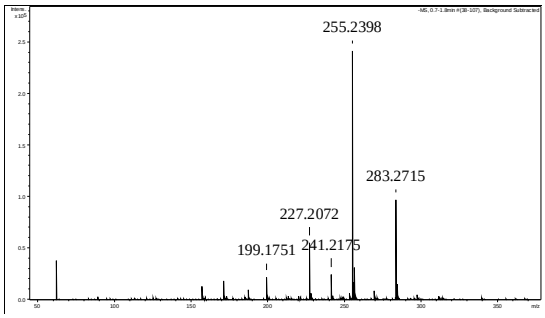

Figure 1: LTP-MS in negative mode of $PM_{2.5}$ filters from Home A in the summertime. Background subtracted.

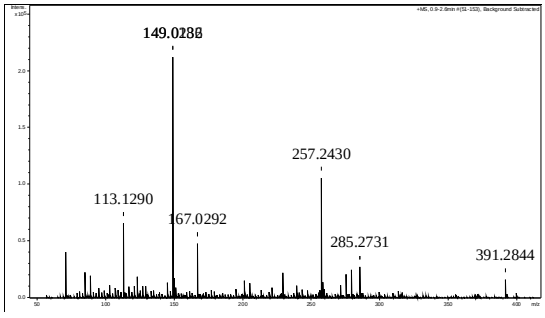

Figure 2: LTP-MS in positive mode of $PM_{2.5}$ filters from Home A in the summertime. Background subtracted.

In positive mode the most abundant peaks in the mass spectrum were *m/z* = 113, 149, 167, 257 285 and 391 as shown in Figure 2. The peaks at *m/z* = 149 and 167 are fragments characteristic to the phthalate backbone ($C_8H_5O_3^+$ and $C_8H_7O_4^+$, respectively). The peaks at *m/z* 113 and 391 are characteristic of di(2-ethylhexyl) phthalate (DEHP) or other phthalates with similar substitution ($C_8H_{17}^+$ and $C_{24}H_{39}O_4^+$ or $[M+H]^+$, respectively). The peak at *m/z* 257 originated from the C_{16} saturated fatty acid, which was also major in negative mode.

The data obtained so far, indicated a difference in the composition between seasons (Spring and summer). An example can be seen in fig 3.

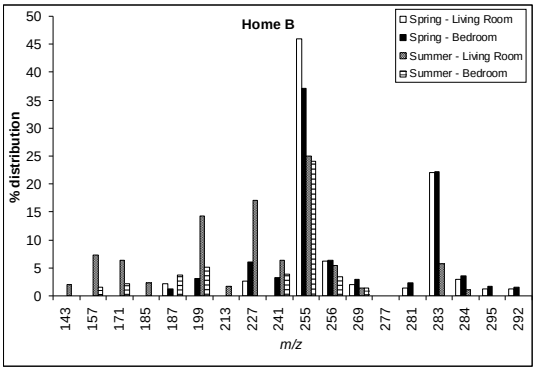

Figure 3: Distribution of dominating compounds in home B.

4 Conclusions

LTP-MS is a promising tool for easy screening of chemical compounds on different surfaces and it can be an interesting method for a number of other applications. The strength of surface analysis is not accurate quantitative determination, but fast screening or finger-printing.

Though LTP can be considered a soft ionization technique, some fragmentation occurs. That enables this method to be used for identification of unknown compounds with MSMS.

5 References

Drake D.R., Brogden K.A.,Dawson, D.V. and Werts P.W. 2008. Antimicrobial lipids at the skin surface. *The Journal of Lipid Research*, 49, 4-11.

Frankel M., Madsen A.M., Hansen E.W. 2011. Influence of Season and Sampling Methods on the Measured Exposure to Indoor Microorganisms and their Inflammatory Potential. *Proceedings of Indoor Air 2011*, Abstract No.: 780

Gustavsen S., Bekö G., Toftum J. and Clausen G. 2011. Field measurements of seasonal variation in air change rate and spatial distribution of gaseous pollutants in five Danish homes. *Proceedings of Indoor Air 2011*, Abstract No.: 608

Harper J.D., Charipar N.A, Mulligan C.C., Zhang X., Cooks R.G. and Ouyang Z. 2008. Low-Temperature Plasma Probe for Ambient Desorption Ionization. *Analytical Chemistry* 80(23), 9097-9104