

Supplement of Atmos. Meas. Tech., 8, 4453–4473, 2015  
<http://www.atmos-meas-tech.net/8/4453/2015/>  
doi:10.5194/amt-8-4453-2015-supplement  
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*Supplement of*

**Ambient measurements of aromatic and oxidized VOCs by PTR-MS and GC-MS: intercomparison between four instruments in a boreal forest in Finland**

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## Supplementary information

### QA/QC for the PTR-MS instruments

When PTR-MS is used for long-term measurements a manual check is done at least once a week to make sure that the measured signals are fine and the instrument is typically calibrated weekly or biweekly.

1. Before calibration it is checked that the actual instrumental parameters are the same as the set values. Also the detector voltage is checked and increased if needed. This is done because the detector sensitivity is decreasing over time. The correct detector voltage is determined by gradually increasing the voltage and observing the voltage at which the instrument response (i.e. signals) plateaus. In practice this is done by increasing the voltage by 50 V steps until the change caused by the increase in detector voltage in the signals is less than 10 %.
2. After the detector voltage has been checked (and adjusted if needed), the instrument is calibrated. Calibration includes measurements of both the BG and a known VOC concentrations of a standard mixture. In order to make sure the lines are clean when BG is measured, zero air is measured first, after which the VOC standard is sampled until the signals plateau (typically 60 minutes). Even though the zero and VOC standard flows are controlled flow controllers when the automatic calibration method is used, both the zero air flow and the VOC standard flows are measured also manually with a flow meter during each calibration.
3. When sensitivities are calculated from the calibration, only the stabilized period is used (see the vertical lines in Figure A1). Suitable BG and calibration standard data are selected manually by the person who does the data analysis. The period is selected so that at least 20 data points are used to determine the average signal.
4. Sensitivities of compounds that are included in the VOC standard, are calculated directly from the calibration. For other compounds, the sensitivities are derived from the relative transmission curve (Figure A2). All the compounds that were considered in this study, were directly calibrated.
5. Once the data selection of step 3 is done, the rest of the data calculation procedure is done with automated Matlab program. The calculation procedure is explained step by step in Taipale et al., 2008.
6. Only data points that were distinct outliers (i.e. single data points that were peaking several orders of magnitude from the rest of the data) or unphysical (i.e. high negative concentration values) were removed from the analysis.

Ideally the PTR-MS instruments would be calibrated e.g. daily. However, it would interfere the measured time series as the calibration takes several hours. The biweekly calibration frequency has been found to be often enough as the normalized sensitivities are not changing very fast. Between July 2011 and August 2015 the PTR-MS2 has been calibrated 95 times using the automatic calibration method. During this time period the average difference of successive normalized sensitivities was less than 1 % for methanol, acetone and benzene, 2 % for acetaldehyde and 13 % for toluene. Histograms of the relative ratio of successive calibrations are shown in Figure A3.

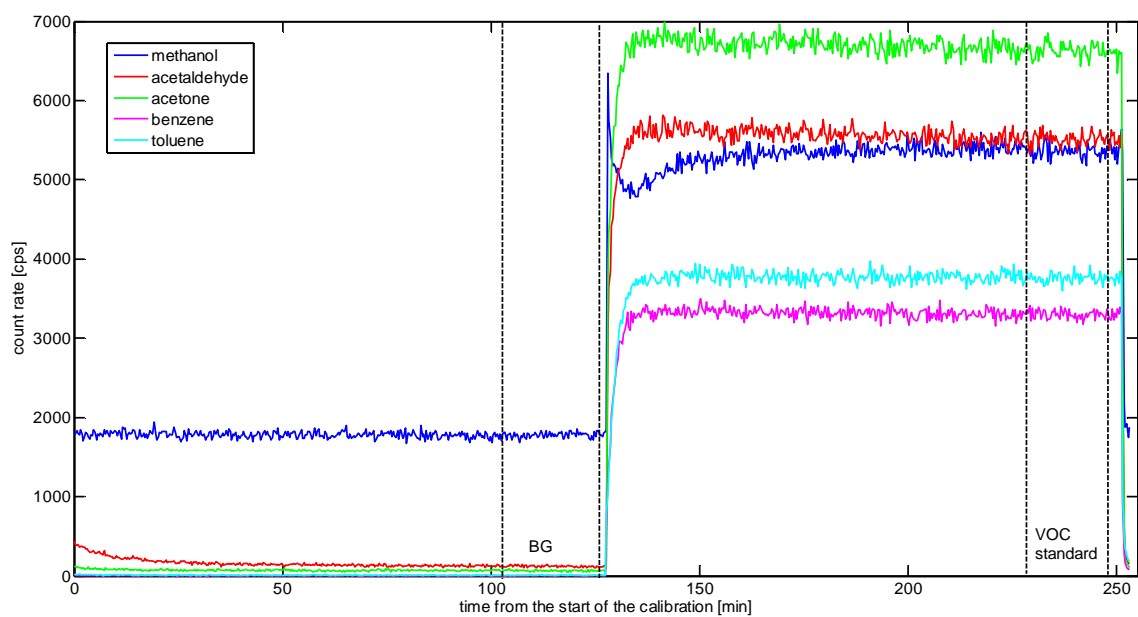


Figure S1. Raw signals of methanol, acetaldehyde, acetone, benzene and toluene measured during one calibration. Dashed vertical lines indicate the time periods used for determining the sensitivities.

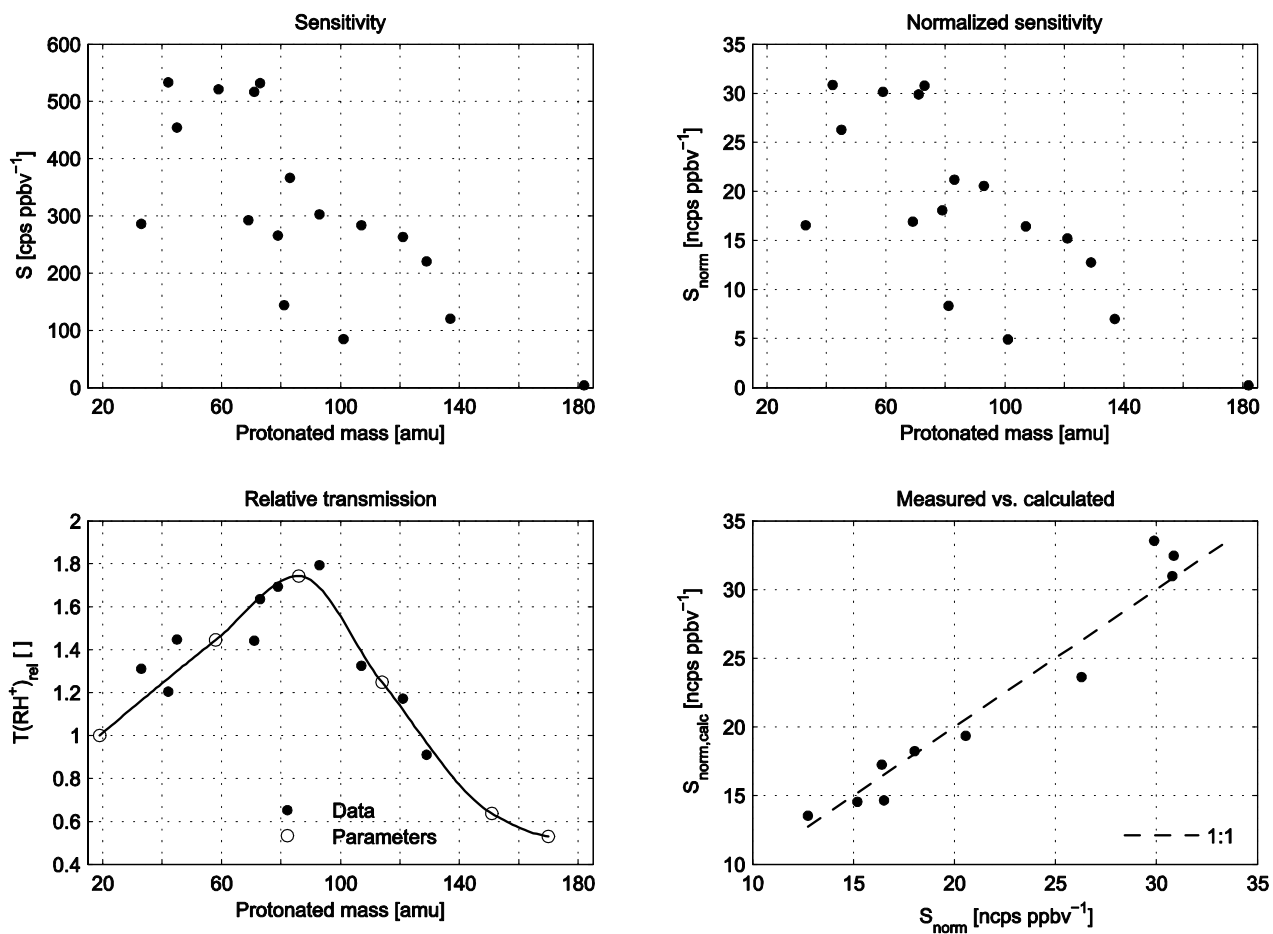


Figure S2. Sensitivities (top left), normalized sensitivities (top right), relative transmission (bottom left) and calculated sensitivities against calculated sensitivities (bottom right) calculated and derived from one calibration.

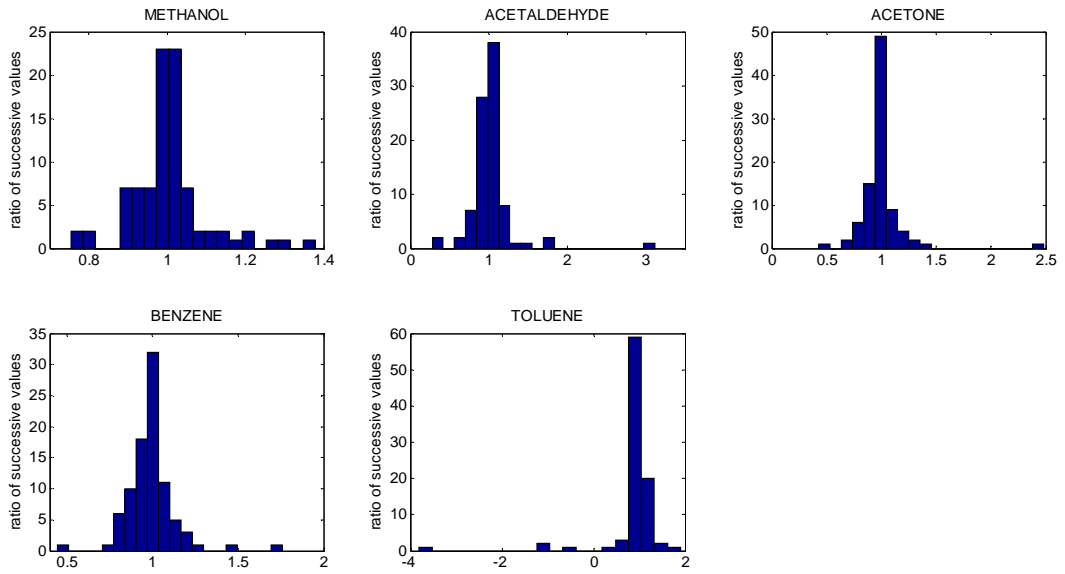
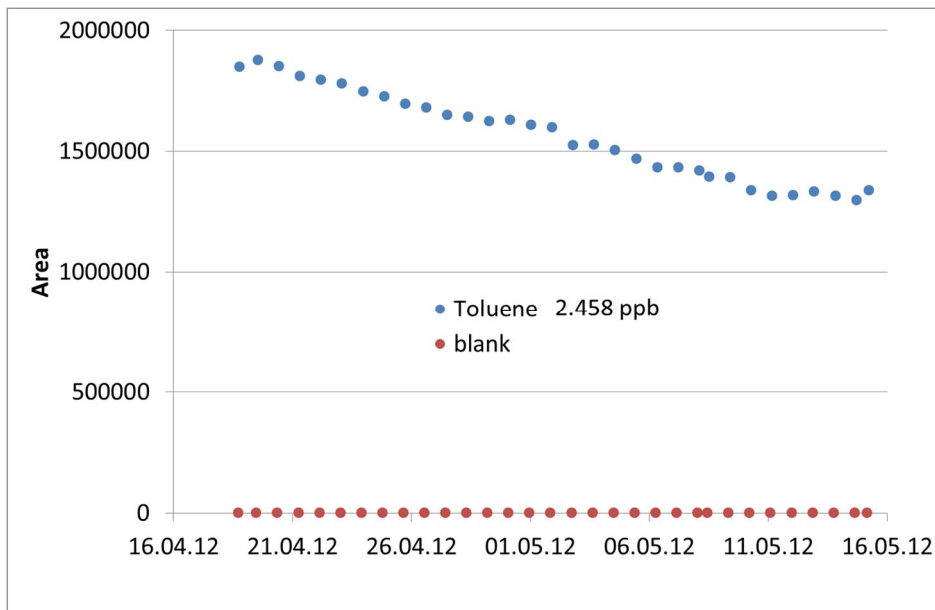
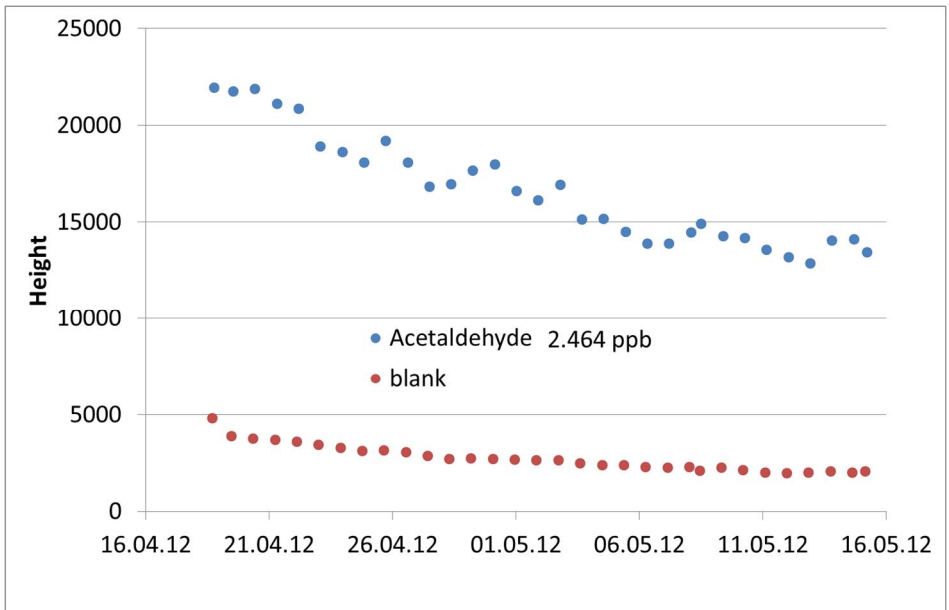
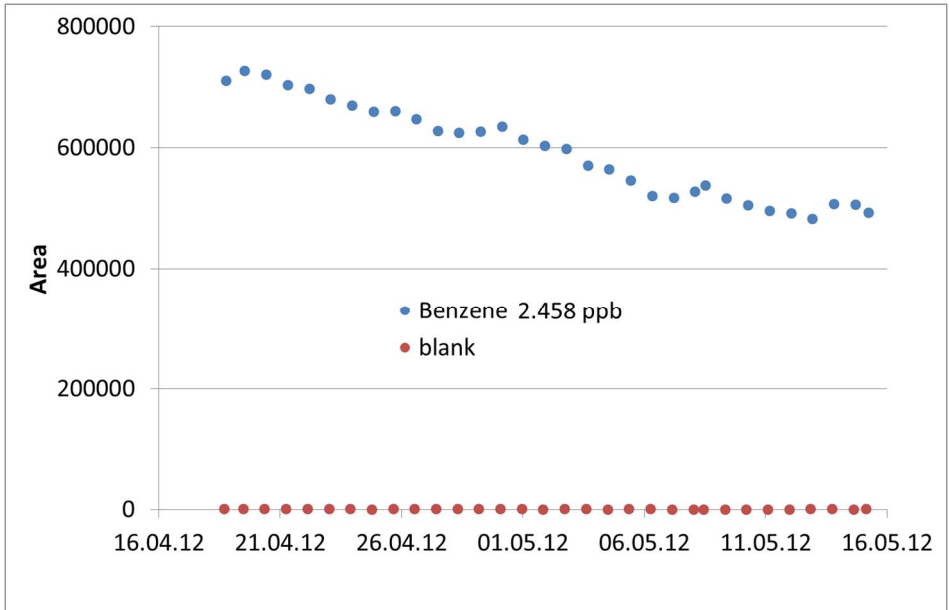


Figure S3. Histograms of the relative sensitivity differences of successive calibrations. In case the value is unity, the sensitivities of the two calibrations were the same.





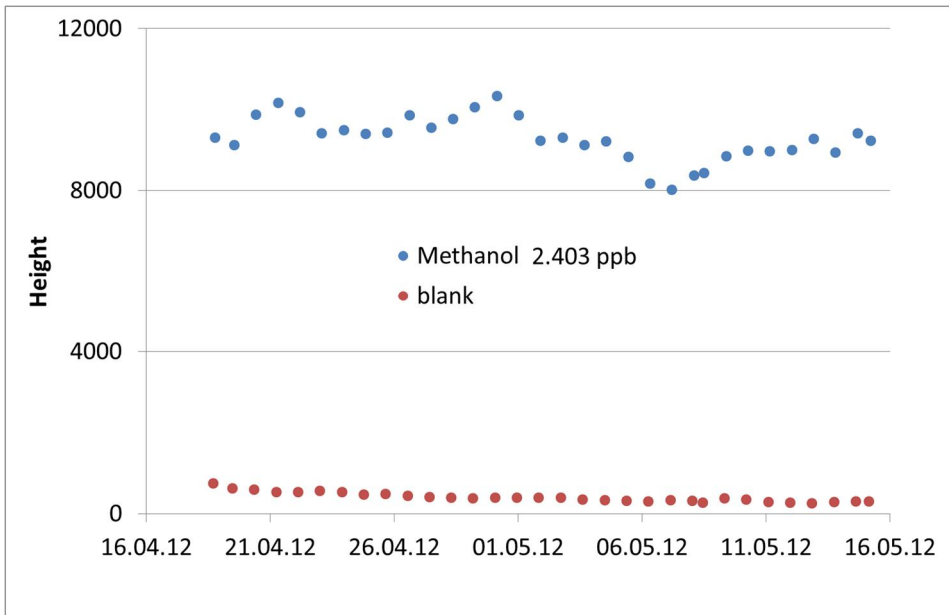
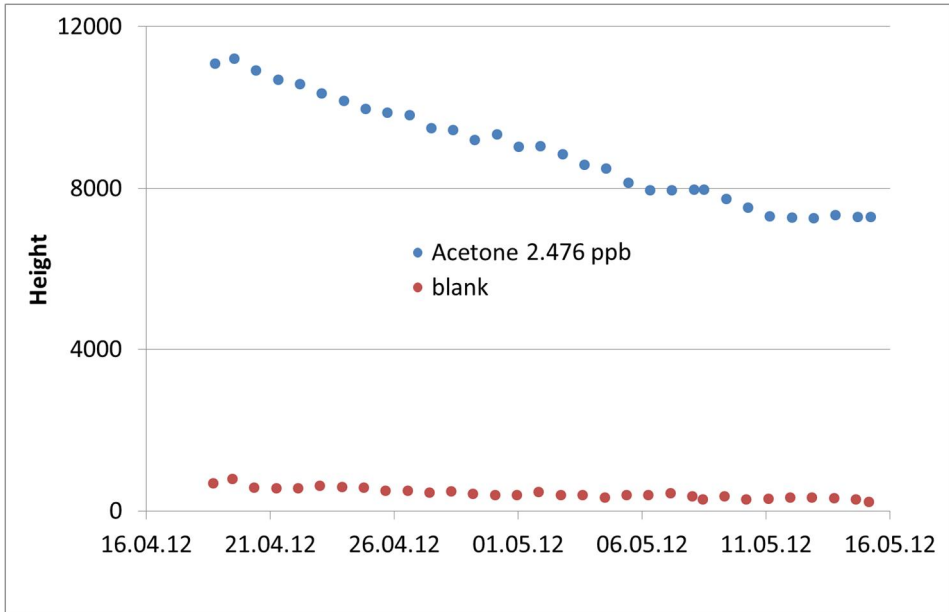


Figure S4: Areas and heights of the daily calibration samples and zero air samples for GC-MS1.

## OA/QC for GC-MS2

GC-MS2 method for acetone, benzene and toluene was validated before the campaign. Desorption efficiency from the cold trap was determined by redesorption after NPL-gas samples. The amount of the sample found in the first desorption was compared to the total amount of the sample from both desorptions. Desorption efficiency for all studied compounds was found to be >97%. Trapping efficiency was checked by flushing the cold trap with clean N<sub>2</sub> (6.0) for 60 minutes after trapping the NPL-gas. Recoveries after flushing were 96, 99 and 98 % for acetone, benzene and toluene, respectively. Blank levels were determined before and after the campaign by heating the cold trap without sampling. Limits of detection were calculated from the standard deviation of the blank or from signal-to-noise ratio. Repeatability was tested by running calibration standard for 15 times. Standard deviations between these 15 analyzes were 7, 1 and 1 % for acetone, benzene and toluene, respectively.

During the campaign calibration standards were analyzed after every 50<sup>th</sup> sample with four different calibration levels and mass spectrometer was tuned at least every two weeks. Tetrachloromethane is known to have very stable mixing ratio in ambient air. It was analyzed from all the ambient air samples and used as a sort of 'internal standard' to see if there were any sampling errors or if the calibration level was shifting.

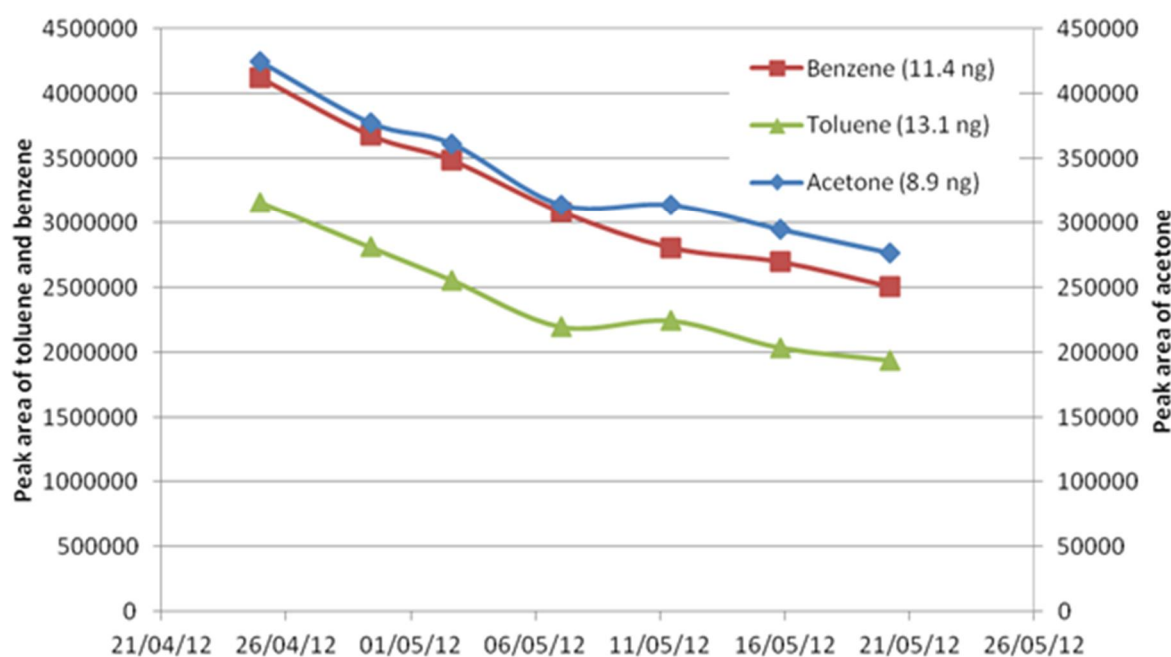


Figure S5: Areas of calibration samples run after every 50<sup>th</sup> sample for GC-MS2.



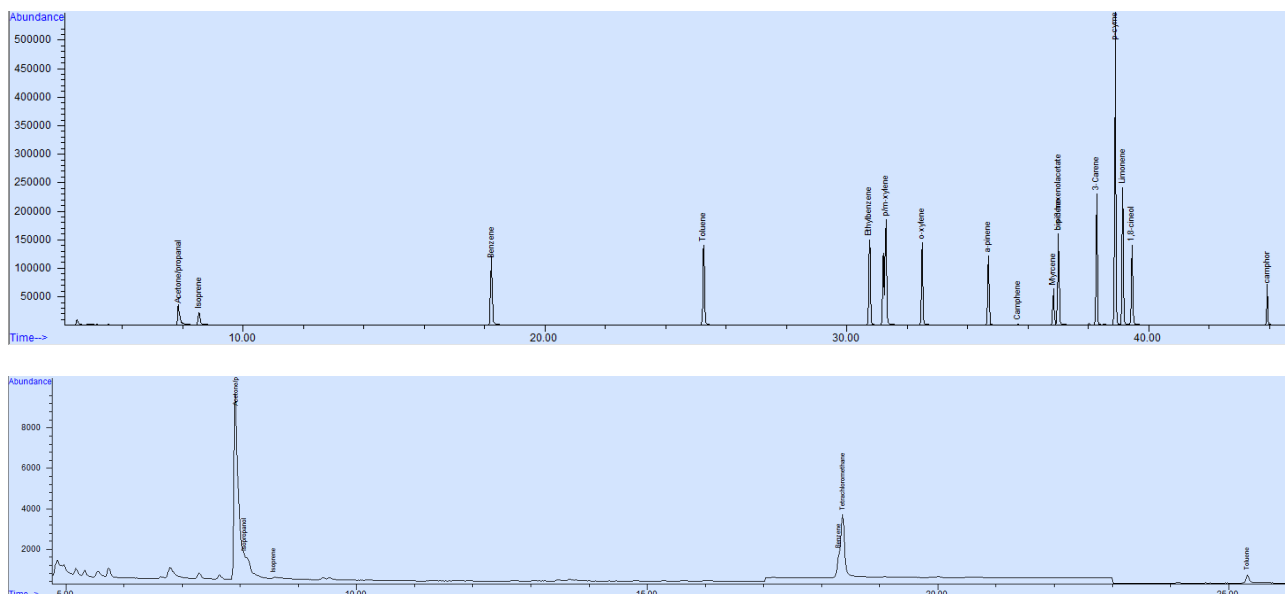


Figure S5. Chromatogram of a calibration standard (upper panel) and a real sample on 16 th of May at 1:00 (lower panel). Isopropanol is coming together with acetone ( $m/z$  58) and tetrachloromethane with benzene ( $m/z$  78), but they do not contain same quantitation ions and therefore this should not be a problem.