Detection efficiency of different compound classes by TD-PTR-MS

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Master thesis

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Contents

Introduction

TD-PTR-MS

A proton transfer reaction mass spectrometer (PTR-MS) produces H_3O^+, which is used to donate a proton to organic compounds to ionize them. Those ions are then accelerated by an electric field, giving all ions with the same charge, the same kinetic energy. Since heavier ions move slower than lighter ones, the time-of-flight of an ion indicates its mass (Holzinger, 2010). Thermal desorption PTR-MS (TD-PTR-MS) is a type of mass spectrometry with which organic compounds in aerosols can be measured. The aerosols are collected on a filter, which is placed in an oven. This oven is connected to the inlet of the PTR-MS. Research on particulate matter is important, because they influence the climate, since particulate matter reflects radiation from the sun and act as cloud condensation nuclei.

Research aim

Some compounds are better detected by the TD-PTR-MS than other compounds. There are multiple reasons for this. When a collision takes place between H_3O^+ and an organic compound, proton transfer always takes place, but different compounds have different probabilities of getting in a collision with a H_3O^+ ion. Another reason is that with some compounds, thermal decomposition occurs in the oven. Furthermore, some compounds fragment upon collision with H_3O^+. Besides these three reasons, there can be other influences as well. The aim of this research is to gain knowledge about the processes that influence the detection efficiency of the TD-PTR-MS of different compound classes, to be able to correct measurements for these processes. This research consists of three parts. In the first part, four alkanes are measured. This is mainly to give insight in the difference between measuring on quartz filter and on aluminium foil. In the second part 33 compounds are measured to provide information on the detectability of different compound classes by the TD-PTR-MS and on processes that occur during those measurements, like fragmentation and the influence of the oven temperature. In the final part, a reference material of a known elemental composition is measured to give information on the detectability of different elements. This reference material is Suwannee River Fulvic Acid Standard I from the International Humic Substances Society.

General methods

This section describes the methods that are used in all three parts of this research. Each part also contains a methods section that describes the methods that are specific for that part only.

The samples

The compounds are first dissolved in a suitable solvent, which varies depending on the solubility of the different compounds. 4 µl of this solution is put on a filter, two minutes before the filter is inserted into the oven system, to allow most of the solvent to evaporate. An exception on this is made when water is used as a solvent, in which case the filter is put in the oven system immediately, for it would take too long to let the water evaporate. Two types of filters are used, quartz filter with a diameter of 5 mm and a piece of aluminium foil of approximately 1 cm^2, which is not a common filter material, but used in this research as an alternative for quartz filter.
Trying out different concentrations learnt that an amount of 5 µg to 35 µg of a compound on a filter usually gives a good result. On some occasions, lower concentrations must be used to prevent the system from getting saturated. Very low concentrations on the other hand can make it hard to identify some fragments, because there signal might then hardly exceed the background noise.
To be able to correct the results for detected ions that are not attributable to the compound, blanks are measured too. Blanks do not have the compound on them, but only 4 µl of solvent. Two replicas are made of the filters with the compound on them and two replicas for the blanks. This results in eight measurements for each compound, namely four with aluminium foil and four with quartz filter. When multiple compounds with the same solvent are measured on the same day, they share the blank measurements.

The oven

The oven runs a 7 step program. After the sample is put in the pre-chamber of the oven, two minutes is waited to let the system stabilize (oven step 0). Then, the sample is put in the oven using a magnet, and an 18 minute program starts, in which the temperature of the oven increases from 50 °C to 350 °C with a 50 °C step every 3 minutes (step 1 - 6). This is illustrated in Table 1. The nitrogen flow that carries the desorbed compound from the oven into the PTR-MS is 200 ml/min. The data is collected in cycles of 5 seconds.

Table 1. Temperature steps of the oven.

Oven step	Temperature (°C)
0	50
1	100
2	150
3	200
4	250
5	300
6	350

Data analysis

The data is processed using a program written in IDL by R. Holzinger. This program calibrates the mass lists and creates a unified mass list for multiple measurements. It also identifies the detected ions and corrects for the system's background signal. For the analysis, a small additional program is written for this work.
A unified mass list is created for each compound. Values of replicas are averaged and the values for the different oven steps are added up resulting in one value for each mass, for each compound. This value is converted from parts-per-billion to nmol. The analysis starts by dividing the detected amount on a sample by the detected amount on the blank and showing only results with a ratio equal or larger than 2 and a minimum value of 1%

of the initial amount of nmol that was put on the filter. Then, manually, results are removed that are not attributable to the compound on the filter. The resulting concentrations are added up. Then the concentrations measured with the blanks are subtracted and this value is divided by the initial amount that was put on the filter. This results in the recovery ratio of the compound.

Part 1 - Alkanes

Methods

Each alkane is solved in acetone. The used alkanes are dodecane ($C_{12}H_{26}$), hexadecane ($C_{16}H_{34}$), octadecane ($C_{18}H_{38}$) and icosane ($C_{20}H_{42}$).

Results

First orientation

348 Different ions are detected. All[1] masses that are detected with a sample/blank ratio of at least 2 and a concentration of at least 0.025 nmol/mol are indicated with a 'x' in the two tables below. *Table 2.* Ions with a relative high concentration on the sample, with only C and H elements. a12 stands for C12H26 on aluminium foil, q12 for C12H26 on quartz filter etc.Table 2 shows all ions with only C and H elements and Table 3 shows the other compounds, which are not attributable to the alkanes.

Table 2. Ions with a relative high concentration on the sample, with only C and H elements. a12 stands for $C_{12}H_{26}$ on aluminium foil, q12 for $C_{12}H_{26}$ on quartz filter etc.

	a12	q12	a16	q16	a18	q18	a20	q20
15.021 CH_2H^+			x		x	x	x	x
27.022 $C_2H_2H^+$			x	x	x	x	x	x
39.023 $C_3H_2H^+$			x		x	x	x	x
41.038 $C_3H_4H^+$			x		x	x	x	x
43.054 $C_3H_6H^+$			x		x	x	x	x
57.070 $C_4H_8H^+$			x		x	x	x	x
71.086 $C_5H_{10}H^+$			x		x	x	x	x
85.102 $C_6h_{13}H^+$			x	x	x	x	x	x
99.119 $C_7H_{15}H^+$			x	x	x	x	x	x
113.128 $C_8H_{17}H^+$			x	x		x		

Table 3. The same as Table 2, but for ions containing also other elements besides C and H.

	a12	q12	a16	q16	a18	q18	a20	q20
57.032 $C_3H_4OH^+$	x		x	x				
59.049 $C_3H_6OH^+$		x						
60.039 $13CC_2H_6OH^+$		x		x				
60.044 $13CC_2H_6OH^+$		x		x				
99.078 $C_6H_{10}OH^+$		x						

$C_nH_{2n}H^+$

It appears from Table 2 that fragments of $C_{12}H_{26}$ are not detected with this approach. This is the case for both aluminium foil and quartz filter.

It also appears from Table 2 that for $C_{16}H_{34}$ on quartz filter, no large concentrations of CH_2H^+, $C_3H_6H^+$, $C_4H_8H^+$ and $C_5H_{10}H^+$ were detected, as opposed to the measurements with $C_{16}H_{34}$ on aluminium foil. A closer look at one of those 'missing masses' is shown in Table 4, where the concentrations of $C_3H_6H^+$ of both replicas are reported for all oven steps.

[1] Everything below m/z 39 is removed, except for 15.021 CH_2H^+ and 27.022 $C_2H_2H^+$, because these removed compounds are attributable to the proton donor H_3O+ or to gasses from the surroundings.

Table 4. $C_{16}H_{34}$ on quartz, detected amount of $C_3H_6H^+$ in nmol.

Oven step	Replica 1	Replica 2
0	0.044	0.414
1	0.975	-0.463
2	0.059	-0.768
3	0.010	-0.643
4	0.002	-0.511
5	-0.001	-0.404
6	0.008	-0.315

It appears from this table that the results for replica two are not as expected, since rather large negative concentrations are measured for steps 1 to 6. Figure 1 and Figure 2 illustrate what happened with replica two. The graph of the first replica (see Figure 1) shows no release of $C_3H_6H^+$ until the first oven step begins. The graph of the second replica (see Figure 2) shows that the $C_3H_6H^+$ is released immediately at the start of the measurement, when the sample is put in the oven, indicating that the oven was not sufficiently cooled down when the sample was inserted. Therefore, the second replica will be removed for further analysis.

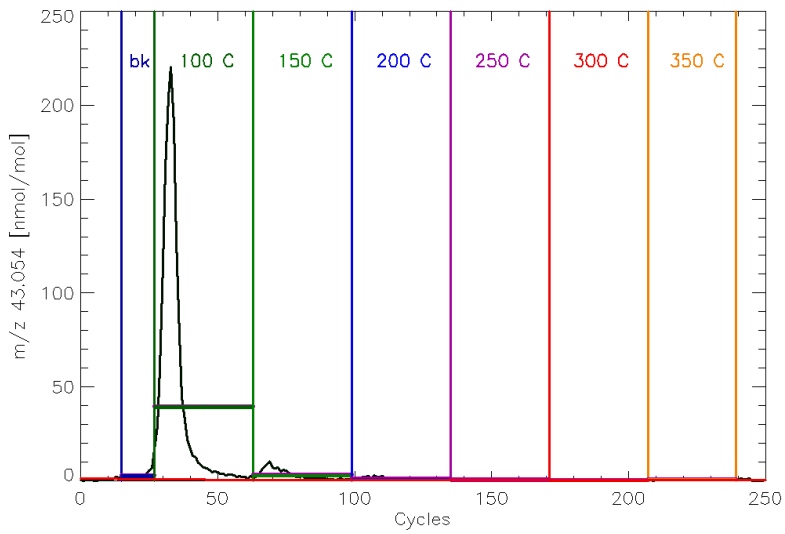


Figure 1. Replica 1 of $C_{12}H_{26}$ on quartz filter. Measured concentration of m/z 43.054 as a function of time.

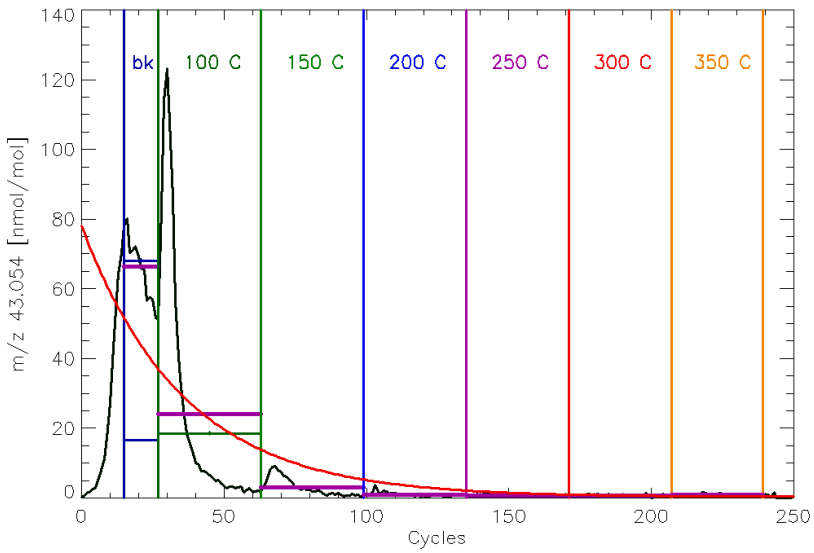


Figure 2. Replica 2 of $C_{12}H_{26}$ on quartz filter. Measured concentration of m/z 43.054 as a function of time.

Table 5 and Table 6 show the detected amounts of the different fragments.

Table 5. Detected amounts of the fragments in nmol for aluminium foil.

Fragment	**Blank**	**$C_{12}H_{26}$**	**$C_{16}H_{34}$**	**$C_{18}H_{38}$**	**$C_{20}H_{42}$**
15.021 CH_2H^+	0.071	0.066	0.193	0.320	0.227
27.023 $C_2H_2H^+$	0.040	0.040	0.162	0.443	0.261
39.023 $C_3H_2H^+$	0.058	0.093	0.688	1.343	0.838
41.039 $C_3H_4H^+$	0.061	0.075	0.727	1.541	1.085
43.054 $C_3H_6H^+$	0.049	0.050	0.422	0.899	0.551
57.070 $C_4H_8H^+$	0.040	0.046	0.600	0.998	0.668
71.086 $C_5H_{10}H^+$	0.017	0.015	0.206	0.347	0.221
85.102 $C_6h_{12}H^+$	0.012	0.010	0.414	0.241	0.160
99.119 $C_7H_{14}H^+$	0.005	0.003	0.061	0.045	0.041
113.128 $C_8H_{16}H^+$	0.005	0.003	0.026	0.022	0.022

Table 6. Detected amounts of the fragments in nmol for quartz filter.

Fragment	**Blank**	**$C_{12}H_{26}$**	**$C_{16}H_{34}$**	**$C_{18}H_{38}$**	**$C_{20}H_{42}$**
15.021 CH_2H^+	0.071	0.087	0.339	0.424	0.247
27.023 $C_2H_2H^+$	0.042	0.052	0.446	0.528	0.277
39.023 $C_3H_2H^+$	0.060	0.095	1.512	1.673	0.804
41.039 $C_3H_4H^+$	0.077	0.108	1.741	1.909	0.982
43.054 $C_3H_6H^+$	0.049	0.069	1.096	1.132	0.524
57.070 $C_4H_8H^+$	0.032	0.061	1.210	1.254	0.585
71.086 $C_5H_{10}H^+$	0.016	0.028	0.439	0.454	0.203
85.102 $C_6h_{12}H^+$	0.012	0.015	0.279	0.317	0.149
99.119 $C_7H_{14}H^+$	0.007	0.016	0.042	0.062	0.037
113.128 $C_8H_{16}H^+$	0.006	0.006	0.019	0.030	0.020

The significance of the differences with the blanks are determined with Student's t-test, with a p-value of 0.05 as the limit. The t-test shows significant increase in the concentrations, compared to the blank, for $C_{16}H_{34}$, $C_{18}H_{38}$ and $C_{20}H_{42}$. However, there is no significant increase for $C_{12}H_{26}$ as can be seen in the t-test results below.

Aluminium foil:

Compound	**t-value**	**p-value**
C12H26	0.0414036	0.967651
C16H34	-3.07010	0.00971507
C18H38	-2.58877	0.0237116
C20H42	-2.56926	0.0245790

Quartz filter:

Compound	**t-value**	**p-value**
C12H26	-0.854473	0.409578
C16H34	-2.54515	0.0256939
C18H38	-2.70126	0.0192644
C20H42	-2.65288	0.0210667

Solvent

The detected concentrations of the 5 compounds that are listed in Table 3 most likely attributable to the solvent acetone.

Below are the measured concentrations of acetone for each temperature step. These are the average values for all aluminium samples on the first row and the average of all quartz samples on the bottom row.

Table 7. Average measured amount of Acetone on aluminium foil and on quartz filter.

Step	0	1	2	3	4	5	6
Aluminium	0.073	0.025	-0.035	-0.040	-0.033	-0.024	-0.011
Quartz	0.089	0.321	-0.066	-0.106	-0.090	-0.069	-0.045

Apart from the negative values, which are caused by automatic background corrections, this shows that during step one, much more acetone was detected from quartz filter, compared to aluminium foil. This indicates that a fraction of the acetone is weakly bound to the quartz filter material and not evaporate until heated during temperature step 1.

Recovery

To determine which fraction of the alkane that is put on the filter is recovered by the TD-PTR-MS, both the initial amount of alkane is calculated and the detected amount is calculated. The detected concentration is determined by adding up the concentrations of the detected ions that are identified above as fragments of alkanes. The assumption is that upon dissociative proton transfer reaction only one fragment of each molecule will be protonated and therefore detected. The results are shown in Table 8.

Table 8. Initial amount and recovery of the alkanes.

Compound	Molar mass [g mol^{-1}]	Mass on filter[µg]	Recovered from aluminium [%]	Recovered from quartz [%]
$C_{12}H_{26}$	170.33	8.39	0.1%	0.4%
$C_{16}H_{34}$	226.45	8.69	1.4%	17.0%
$C_{18}H_{38}$	254.50	4.97	30.1%	37.9%
$C_{20}H_{42}$	282.55	2.52	42.0%	39.1%

It appears that $C_{12}H_{26}$ is hardly recovered by the TD-PTR-MS. It is likely that the $C_{12}H_{26}$ is already evaporated before the measurement starts. More $C_{12}H_{26}$, $C_{16}H_{34}$ and $C_{18}H_{38}$ is recovered on quartz than on aluminium, indicating that on quartz, a smaller fraction evaporates before the measurement than on aluminium. So for compounds that relatively easy evaporate, quartz filter seems more suitable than aluminium foil. For $C_{20}H_{42}$ however, higher concentrations are measured on aluminium. This indicates that aluminium makes it easier for heavier molecules to desorb than quartz.
The highest recovery is 42%. This might indicate that a lower reaction rate constant should be used. However, this seems not the case, since the used reaction rate constant is 3e-9 cm^3s^{-1}, and Spanel and Smith (1998) report a constant of 2.8 e-9 cm^3s^{-1} for dodecane ($C_{12}H_{26}$). Longer alkanes have even higher reaction rate constants, so the used constant seems appropriate.

Temperature

Table 9 shows at which temperature steps the alkanes are detected. The number in the table indicates the percentage that is detected in that temperature step, compared to the total amount. The results for $C_{12}H_{36}$ are not as expected. This is because this compound was hardly detected at all. The other compounds show that longer alkanes are more detected at higher temperatures. They also show that on aluminium foil, slightly more is detected at lower temperatures. This indicates that alkanes desorb easier from aluminium foil than from quartz filter.

Table 9. Detection ratios at each temperature step. A12 means $C_{12}H_{26}$ on aluminium etc.

Temp. [°C]	A12	Q12	A16	Q16	A18	Q18	A20	Q20
50	-1	0	6	0	0	0	0	0
100	14	38	92	92	89	87	49	47
150	21	26	2	6	7	10	43	45
200	15	18	0	1	3	2	5	6
250	19	8	0	0	1	1	2	2
300	6	5	0	0	0	0	1	1
350	26	5	0	0	0	0	0	0

Conclusions

The detected fraction is higher for longer alkanes, with 42% being the highest detected fraction. $C_{12}H_{26}$ is hardly detected because it is probably already evaporated before the measurement starts. $C_{16}H_{34}$, $C_{18}H_{38}$ and $C_{20}H_{42}$ fragment into $C_nH_{2n}H^+$ and $C_2H_2H^+$, $C_3H_2H^+$ and $C_3H_4H^+$ ions. $C_{12}H_{26}$, $C_{16}H_{34}$ and $C_{18}H_{38}$ are more detected on quartz than on aluminium, indicating that from quartz, a smaller fraction evaporates before the start of the measurement, than from aluminium. So for compounds that relatively easy evaporate, quartz filter is more suitable than aluminium foil. For $C_{20}H_{42}$ however, higher concentrations are measured on aluminium. This indicates that aluminium makes it easier for heavier molecules to desorb, compared to quartz. $C_{16}H_{34}$ and $C_{18}H_{38}$ are mainly detected during the 100°C temperature step and $C_{20}H_{42}$ during the 100°C and 150°C temperature steps. So the longer the alkane, the higher the temperature at which it is detected. On quartz filter, the alkanes are detected slightly more at a higher temperature, compared to aluminium foil.

Part 2 - Various compounds

Methods

Data collection
33 compounds are measured with a TD-PTR-MS. These compounds are chosen because they are used in earlier research (Aiken et al., 2008). All substances are supplied by Sigma-Aldrich and have purities greater than 98%, except for nonyl aldehyde and glutaric anhydride, which have a purity of 95%, and for benzoyl peroxide that has, for safety reasons, a purity of 75%. The setup is the same as in part 1 of this research. 18 compounds were dissolved in deionized water (MiliQ), 12 in ethanol and 3 in acetone. Appendix 1 shows the solvent for each compound. 4 µl of the solution was put on the filter, corresponding to 10 µg of the compound on the filter. 1 µl was used for fluoranthene (nr. 28), because with 4 µl, the concentration was too high, causing a depletion of priming ions in the PTR-MS.

Results

Table 10 shows the recovery rate, temperature at which the compound is detected and the real and measured O/C, N/C and H/C values. For the calculation of these ratios, fragments that were not identified had to be left out. All detected fragments are listed in Appendix 1.

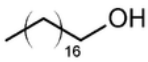
Table 10. Results of 33 compounds. R. Q and R. A stand for recovery from quartz filter and recovery from aluminium foil. R. O/C and M. O/C stand for real O/C and measured O/C. The same goes for N/C and H/C.

Number; formula Name	CAS-Nr. Mol. weight (g/mol)	R. Q R. A	Temp quartz	R. O/C M. O/C	R. N/C M. N/C	R. H/C M. H/C
1 $C_{18}H_{38}O$ 1-Octadecanol	112-92-5 270.49	23 36	150 (70%)	0.06 0.00		2.11 1.57
2 $C_9H_{18}O$ Nonyl aldehyde	124-19-6 142.24	54 19	50 (63%)	0.11 0.02		2.00 1.59
3 $C_8H_5NO_2$ Phthalamide	85-41-6 147.13	120 132	100 (14%), 150 (72%)	0.25 0.21	0.13 0.12	0.63 0.57
4 $C_{20}H_{24}N_2O_2$ Quinine	130-95-0 324.42	0 0				
5 $C_2H_5NO_2$ Glycine	56-40-6 75.07	12 1	150 (16%), 200 (53%), 250 (16%)	1.00 0.55	0.50 0.59	2.50 3.49
6 $C_3H_7NO_2$ Alanine	56-41-7 89.09	3 35	150 (6%), 200 (21%), 250 (23%)	0.67 0.02	0.33 0.50	2.33 2.00
7 $C_3H_7NO_3$ Serine	56-45-1 105.09	6 2	200 (37%), 250 (26%)	1.00 0.00	0.33 0.50	2.33 1.92
8 $C_4H_7NO_4$ Aspartic acid	56-84-8 133.10	? ?	250 (19%), 300 (40%), 350 (29%)	1.00 0.62	0.25 0.12	1.75 0.69
9 $C_4H_9NO_2$ Aminobutyric acid	56-12-2 103.12	118 106	150 (22%), 200 (27%), 250 (21%)	0.50 0.25	0.25 0.25	2.25 1.74
10 $C_4H_9NO_3$ Threonine	72-19-5 119.12	80 34	150 (5%), 200 (40%), 250 (26%)	0.75 0.49	0.25 0.05	2.25 1.97
11 $C_5H_{11}NO_2S$ Methionine	63-68-3 149.21	13 7	200 (33%), 250 (13%), 300 (23%)	0.40 0.00	0.20 0.00	2.20 4.00
12 $C_5H_9NO_4$ Glutamic acid	56-86-0 147.13	? ?	50 (13%), 200 (18%), 350 (30%)	0.80 0.25	0.20 0.25	2.10 1.39
13 $C_6H_{13}NO_2$ Leucine	61-90-5 131.17	13 1	200 (8%), 250 (24%), 300 (34%)	0.33 0.11	0.17 0.21	2.17 2.21

14 $C_6H_{13}NO_2$ Isoleucine	73-32-5 131.17	8 16	200 (17%), 300 (29%), 350 (30%)	0.33 0.15	0.17 0.12	2.12 1.83
15 $C_7H_7NO_2$ 4-Aminobenzoic acid	150-13-0 137.14	78 112	 150 (43%), 200 (28%)	0.29 0.22	0.14 0.15	1.00 0.97
16 $C_9H_{11}NO_2$ Phenylalanine	63-91-2 165.19	? ?	100 (11%), 300 (20%), 350 (32%)	0.22 0.46	0.11 0.12	1.22 1.49
17 $C_9H_{11}NO_3$ Tyrosine	60-18-4 181.19	0.3 0.1	 300 (28%), 350 (76%)	0.33 0.15	0.11 0.00	1.22 1.05
18 $C_{11}H_{12}N_2O_2$ Tryptophan	73-22-3 204.23	14 10	250 (6%), 300 (42%), 350 (51%)	0.18 0.00	0.18 0.12	1.09 0.90
19 $C_5H_6O_3$ Glutaric anhydride	108-55-4 114.10	82 83	100 (11%), 150 (59%), 200 (13%)	0.60 0.52		1.20 1.40
20 $C_6H_{10}O_5$ Levoglucosan	498-07-7 162.14	27 20	150 (15%), 200 (38%), 250 (20%)	0.85 0.42		1.67 1.03
21 $C_{10}H_{20}O_2$ Decanoic acid	334-48-5 172.26	73 63	 100 (59%), 150 (17%)	0.20 0.18		2.00 1.97
22 $C_{15}H_{30}O_2$ Pentadecanoic acid	1002-84-2 242.40	95 126	150 (48%), 200 (16%), 250 (11%), 300 (10%)	0.13 0.13		2.00 1.99
23 $C_{18}H_{36}O_2$ Stearic acid	57-11-4 284.48	74 110	150 (15%), 200 (32%), 250 (19%), 300 (13%)	0.11 0.11		2.00 2.00
24 $C_5H_8O_4$ Glutaric acid	110-94-1 132.11	75 68	 100 (13%), 150 (58%)	0.80 0.52		1.60 1.40
25 $C_6H_{10}O_4$ Adipic Acid	124-04-9 146.14	52 39	 150 (58%), 200 (17%)	0.67 0.15		1.67 1.55
26 $C_{24}H_{38}O_4$ Dioctyl phthalate	117-81-7 390.56	38 33	200 (23%), 250 (31%), 300 (27%), 350 (15%)	0.17 0.22		1.58 1.31
27 $C_{12}H_9N$ Carbazole	86-74-8 167.21	67 117	 150 (84%)		0.08 0.08	0.75 0.75
28 $C_{16}H_{10}$ Fluoranthene	206-44-0 202.25	201 158	 100 (51%), 150 (42%)			0.63 0.63
29 $C_{16}H_{10}$ Pyrene	129-00-0 202.25	256 309	 100 (41%), 150 (45%)			0.63 0.63
30 $C_{14}H_{10}O$ Anthrone	90-44-8 194.23	101 129	 150 (70%), 200 (13 %)	0.07 0.07		0.71 0.71
31 $C_{14}H_{10}O_4$ Benzoyl peroxide	94-36-0 242.23	234 195	 100 (41%), 150 (28%)	0.29 0.22		0.71 0.81
32 $C_6H_5NO_2$ Nicotinic acid	59-67-6 123.11	75 100	150 (29%), 200 (24%), 250 (18%)	0.33 0.32	0.17 0.17	0.83 0.81
33 CH_4O_3S Methanesulfonic acid	75-75-2 96.11	0 0				

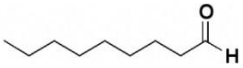
A short description of the peculiar results of each compound will now be given.

1. $C_{18}H_{38}O$ - 1-Octadecanol



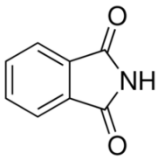
The choice of filter material is of influence on the temperature at which 1-octadecanol is detected. On aluminium foil, 66% is detected at the 100°C step and 26% at the 150°C step. On quartz filter, only 13% is detected at the 100°C step and 70 % at the 150°C step. 1-Octadecanol is recovered about 50% more from aluminium foil than from quartz filter. $C_{18}H_{38}O$ is detected only as fragments consisting of C and H, with $C_8H_{16}H^+$ being the largest detected fragment. Also, smaller fragments are more often detected than larger ones.

2. $C_9H_{18}O$ - Nonyl Aldehyde



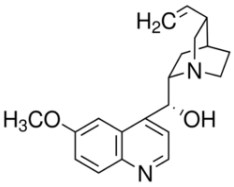
Nonyl aldehyde is detected on quartz filter almost three times more than on aluminium foil. It is also detected at higher temperatures on aluminium foil. About 10% of the detected ions are the complete protonated molecule. All other ions are fragments consisting of only C and H elements.

3. $C_8H_5NO_2$ - Phthalamide



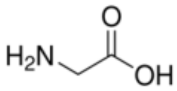
Phthalamide is recovered very well, there is no loss of this compound. It is mainly detected as the protonated complete molecule (72%) and for 22% as the protonated complete molecule missing two H atoms and an O atom.

4. $C_{20}H_{24}N_2O_2$ - Quinine



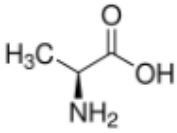
Quinine is not detected. This is not due to the molecular weight, for another heavier molecule is detected by the PTR-MS (Dioctyl phthalate). Quinine does have the highest boiling point (496 °C) of all measured substances, but no direct relation can be discovered between the boiling points of the substances and their recovery and temperature at which they are recovered.

5. $C_2H_5NO_2$ - Glycine



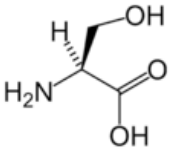
Only a small fraction of glycine is recovered, and 17 times more on quartz then on aluminium. On quartz, the most detected fragment is m/z 32.050 CH_5NH^+ (60%). On aluminium foil, this is the only detected ion. On quartz, the protonated $C_2H_5NO_2$ molecule (m/z 76.040) is also detected and a fragment that lost a N and H atom (m/z 61.029, $C_2H_4O_2$) . The different ions are detected at different temperatures. $C_2H_4O_2$ is detected at 150°C and CH_5NH^+ at 200°C. The detection of fragments at different temperatures indicates disintegration of the substance in the oven. $C_2H_5NO_2H^+$ is detected at a rather constant rate during all temperatures, which can be caused by a relative cold point in the system, causing the substance to condensate.

6. $C_3H_7NO_2$ - Alanine



The molecule structure of alanine resembles glycine, with the difference that alanine features an alkyl group. This has a large influence as can be seen in the results. Alanine is recovered on aluminium much better than on quartz. The complete $C_3H_7NO_2$ molecule is not detected. The fragments that are most detected (about 80%) are $C_2H_3NH^+$ and C_2H_5N H^+, resulting in a very low detected O/C ratio. 18% of the detected amount belongs to unidentified fragments.

7. $C_3H_7NO_3$ - Serine

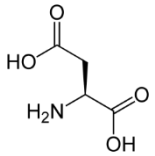


Serine is hardly detected, but more on quartz filter than on aluminium foil. One of the three detected fragments is not identified (m/z 70.075). The other two fragments consist of only C, H and N elements. Detection starts at 200°C, but substantial amounts are detected until the end of the measurement, indicating either that serine desorbs very slow, or that a cold point in the system causes the desorbed serine to condense.

8. $C_4H_7NO_4$ - Aspartic Acid

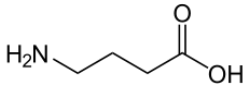
Due to a mistake the recovery ratio can not be determined for aspartic acid. The mistake was that this compound came in a container with only 1 ug of the compound. The solution was made in this container, but the compound was not completely soluted and therefore the

solution was retrieved from the original container to be diluted in another container. Due to the small size of the opening of the original container, some of the solution was spilled during this process.
Like glycine (nr. 5), fragments are detected at different temperatures. The two compounds are not measured at the same day, ruling out an accidental cold point in the system. Fragments $C_4H_3O_2NH^+$ (m/z 98.024) and $C_4H_5O_2NH^+$ (m/z 100.042) are detected at 300°C, although on quartz, about 10% is already detected at 250°C. Fragment $C_4H_2O_3H^+$ (m/z 99.009) is detected at 200°C, but also at the higher temperatures. An unidentified fragment with m/z 130.052 is detected at all temperature steps. This is consistent amongst all replicas.



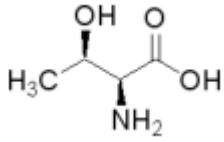
9. $C_4H_9NO_2$ - Aminobutyric Acid

92% of the aminobutyric acid is recovered, both from aluminium foil and quartz filter, so there is no substantial loss. Detections of aminobutyric acid starts at 150°C. With aluminium foil, 84% is detected at 150°C and 200°C, whereas on quartz filter, only 49% is detected at these temperatures while the rest is detected at higher temperatures. This indicates that aminobutyric acid evaporates much easier from aluminium than from quartz filter. Fragment $C_4H_7NOH^+$ contributed for 98% to the detected signal, which halves the O/C ratio.



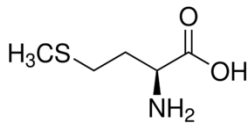
10. $C_4H_9NO_3$ - Threonine

Threonine is recovered on quartz filter more than twice as much as on aluminium foil. On quartz filter, the temperature step with the highest measured amount is at the 200°C step, while on aluminium, this was at the 250°C step. 21 different ions are detected, with m/z 45.034 $C_2H_4OH^+$ contributing for about 50% to the total recovered amount. This results in a low N/C ratio. 9% of the detected amount belongs to unidentified fragments.



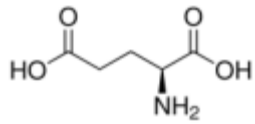
11. $C_5H_{11}NO_2S$ - Methionine

Methionine is detected, but only a small amount. The only detected ion is m/z 49.012, which is not identified, but probably CSH_4H^+.



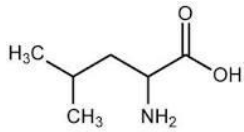
12. $C_5H_9NO_4$ - Glutamic Acid

Due to a mistake (the same as with number 8) the recovery ratio can not be determined for glutamic acid. Three different fragments are detected, of which one is not identified. The two identified fragments both lost three out of four oxygen atoms and only one carbon atom. This results in a much lower measured O/C ratio. Twice as much is detected at quartz filter, compared to aluminium foil.



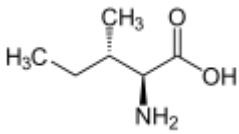
13. $C_6H_{13}NO_2$ - Leucine

The fragment that is detected most is $C_5H_{11}NH^+$, so the molecule lost the carboxyl group. $C_2H_5NH^+$ is detected too, which implies that the upon protonation, the molecule breaks up at two points to form $C_2H_5NH^+$. Leucine is detected in different temperature steps in about equal amounts instead of being detected in mainly one oven step. There was also still some leucine detected at the next measurement. This might indicate recondensation.



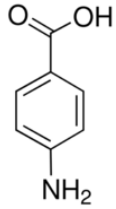
14. $C_6H_{13}NO_2$ - Isoleucine

With quartz filter, four detected ions have a higher mass than the original molecule (m/z 154.158, 200.161, 210.151 and 227.178). It is not likely that the solution is contaminated, because on aluminium foil, which was measured after quartz, only two of those ions were detected



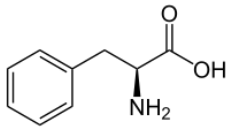
in substantial amounts. It is also not likely that the system was contaminated, because during the former measurement, those ions where not detected. Therefore, this indicates oligomerization.
A remarkable difference between quartz filter and aluminium foil is that the protonated complete molecule is detected rather well on aluminium foil, but on quartz filter only about 1% of that amount.

15. $C_7H_7NO_2$ - 4-Aminobenzoic Acid



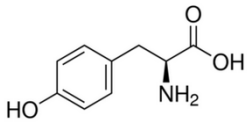
4-Aminobenzoic acid is recovered very well and a bit more on aluminium foil than on quartz filter. The substance is mainly detected as the protonated complete molecule (66%), but also as two fragments. One fragment lost an O and two H atoms and the other a C and two O atoms, which is the carboxyl group.

16. $C_9H_{11}NO_2$ - Phenylalanine



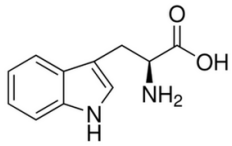
Due to a mistake (the same as with number 8) the recovery ratio can not be determined for phenylalanine. Three detected ions have higher masses than the original molecule. The heaviest of those three ions is not detected on aluminium foil. Fragments 44.049 $C_2H_5NH^+$ and 86.105 $C_3H_3O_2NH^+$ are immediately detected when the sample is put in the pre-chamber of the oven, where the temperature is 50°C at most. Fragment 91.057 $C_7H_6H^+$ is detected at the 300°C step though.

17. $C_9H_{11}NO_3$ - Tyrosine



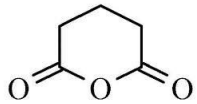
Tyrosine is hardly detected. 32% of the detected amount belongs to an unidentified fragment. The other three fragments are 95.048 $C_6H_6OH^+$, 109.065 $C_7H_8OH^+$ and 121.064 $C_8H_8OH^+$. So most likely, the fragments still contain the aromatic ring.

18. $C_{11}H_{12}N_2O_2$ - Tryptophan



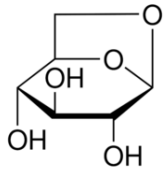
Tryptophan is detected as two different fragments (m/z 118.073 $C_8H_7NH^+$ and m/z 132.086 $C_9H_9NH^+$), both without the O elements and one N element. It is therefore likely that both fragments still contain the aromatic hydrocarbon.

19. $C_5H_6O_3$ - Glutaric Anhydride



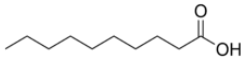
Glutaric anhydride is detected well. The most detected ion is m/z 87.044 $C_4H_6O_2H^+$ (43%).

20. $C_6H_{10}O_5$ - Levoglucosan



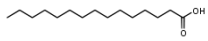
Levoglucosan is detected as the protonated complete molecule and as 16 different fragments, of which m/z 85.028 $C_4H_4O_2H^+$ is the most detected one (about 1/3 of the total detected amount).

21. $C_{10}H_{20}O_2$ - Decanoic Acid



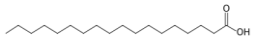
Decanoic acid is the shortest one in a series of three alkanoic acids. Like the other two, it is detected rather well.

22. $C_{15}H_{30}O_2$ - Pentadecanoic Acid



Pentadecanoic acid has, apart from the protonated complete molecule, mostly the same fragments as decanoic acid, which consist of only C and H elements.

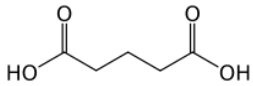
23. $C_{18}H_{36}O_2$ - Stearic Acid



Like the other two alkanoic acids, Stearic acid is mainly detected as the complete protonated molecule. Comparing the temperatures at which

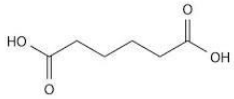
the alkanoic acids are detected shows that a longer molecule is detected at a higher temperature.

24. $C_5H_8O_4$ - Glutaric Acid



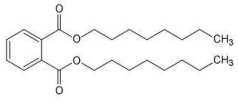
Glutaric acid is recovered well. It is detected as four different fragments, of which m/z 87.043 $C_4H_6O_2H^+$ is the most detected one (46%). This is the complete molecule without one of the carboxyl groups.

25. $C_6H_{10}O_4$ - Adipic Acid



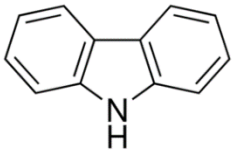
It is detected only as fragments, which contain relatively few O elements, resulting in an O/C ratio which is less than one third of the original value. One remarkable ion was detected, which is almost two times heavier than the original molecule. This ion is m/z 285.281, which is identified as $C_{18}H_{36}O_2H^+$. This is the most detected ion and the total amount weights 21% of the weight that is put on the filter. It is most detected at the same temperature as the other fragments (150°C), but also at other temperatures.

26. $C_{24}H_{38}O_4$ - Dioctyl Phthalate



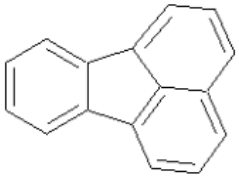
This is the heaviest compound that is measured in this research, with a molecular weight of 390.56 gram/mol. About 35% is recovered. Dioctyl phthalate is detected as the complete protonated molecule, but also as fragments.

27. $C_{12}H_9N$ - Carbazole



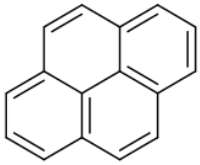
Carbazole is detected as the protonated complete molecule. It is better recovered from aluminium foil. On quartz filter, it is not detected until the 150°C step, but on aluminium foil, 30% is already detected at the 100°C step. One replica of carbazole on aluminium is not used in the analysis, for its H_3O^+ level was abnormal.

28. $C_{16}H_{10}$ - Fluoranthene



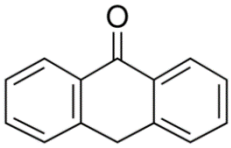
Fluoranthene has a high recovery ratio. This compound is detected as the protonated complete molecule and not as fragments, so the high recovery is not caused by disintegration of the molecule in the oven.

29. $C_{16}H_{10}$ - Pyrene



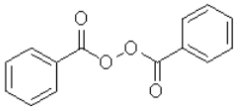
Pyrene is recovered best of all measured compounds, with recovery ratios of 256% on quartz filter and 309% on aluminium foil. It is only detected as the protonated complete molecule.

30. $C_{14}H_{10}O$ - Anthrone



Anthrone is mostly detected as the protonated complete molecule (63%). The other part is detected as m/z 209.060. This is higher than the molecular mass of the original molecule, which is 194.23 g/mol. This ion is not identified.

31. $C_{14}H_{10}O_4$ - Benzoyl Peroxide

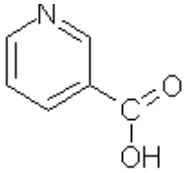


Benzoyl Peroxide is recovered at high ratios. It is only detected as fragments of maximum half the weight of the original molecule.

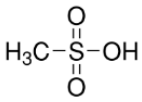
32. $C_6H_5NO_2$ - Nicotinic Acid

Nicotinic acid is released from aluminium foil quicker than from quartz filter. With aluminium foil, 59% of the total signal is detected during the 150 °C step, whereas on quartz only 29% is detected during this oven

step. Nicotinic Acid is mainly (93%) detected as the protonated complete molecule.



33. CH_4O_3S - Methanesulfonic Acid



This compound is not detected by the TD-PTR-MS. The reason for this is not clear.

Conclusions

Detection

2 out of 33 substances are not detected. With 12 compounds, the recovery was better from aluminium. With 16 compounds, the recovery was better from quartz.
The temperature at which a compound is detected can differ with different filter materials. 8 Compounds are more detected at lower temperatures on quartz, but 18 compounds are on aluminium foil more detected at a lower temperature. The other compounds show no clear difference.
In three cases (compounds 14, 25 and 30) one or more ions are detected that have a higher mass than the protonated original molecule, indicating oligomerization. Apparently the molecules of these compounds react with themself when heated.

Elemental composition

Of the 28 compounds containing oxygen that are detected, only 2 are detected with a higher O/C ratio than the original molecule (compounds 16 and 26) and 3 compounds are detected with the original O/C ratio. So 23 compounds are detected with a lower O/C ratio. 20 out of 31 compounds have a lower detected H/C ratio and 6 have a higher H/C ratio than the original molecule. Nitrogen on the other hand is as often detected at a higher ratio as at a lower ratio.

Fragmentation

Only three compounds do not fragment at all. Often, when a molecule breaks up into a part with oxygen and a part without, the part without the oxygen gets protonated, examples are compounds 1, 2, 21 and 22. It also often happens that a fragment consists of the original molecule missing one O and two H atoms (compounds 3, 9, 15, 21 and 22) or a carboxyl group (compounds 5, 7 and 13). The 5 carboxylic acids are detected rather well. Remarkable is the difference between carboxylic acids with one and two carboxyl groups. Molecules with one carboxyl group are mainly detected as the complete protonated molecule, whereas the ones with two carboxyl groups are only detected as fragments.
Aromatic hydrocarbons seem to stay intact upon protonation.
15 Amines are measured. 10 Amines are only detected as fragments and 4 mainly as fragments. Only compound 15, 4-Aminobenzoic Acid, is mainly (66%) detected as the protonated complete molecule.

Solvents

While working on part 3 of this research, it became clear that the effect of water on the measurement was underestimated. When calculating the decrease of H_3O^+, using isotope 21.021, it became clear that all, except one, of the compounds that are solved in water, have one or more replicas that suffer a decrease of H_3O^+ of at least 30% compared to the maximum concentration of H_3O^+ during the measurement. This decrease is only for about one minute after the oven program is started, after which the H_3O^+ level is stable again. Therefore, the effect on the results is small, especially when considering that very few material of the measured compounds is detected at that temperature step. Still, it might be a small improvement to make sure all water is evaporated when the oven program starts. All used measurements with other solvents have a decrease of H_3O^+ of less than 13%.

Part 3 - Reference material

Methods

The reference material that is used is Suwannee river fulvic acid standard I from the International Humic Substances Society. The elemental composition is shown in table 13, expressed in H/C, O/C and N/C ratios. Four solutions are made, each with 5 mg fulvic acid solved in 1 ml deionised water. In three of the four solutions, 10 mg of a salt is added. The salts that are used are ammonium sulfate, ammonium nitrate and ammonium bisulfate. 20 µl of the solution is put on the filter, which corresponds to 100 µg of fulvic acid. The used filter material is aluminium foil, in pieces of approximately 1cm x 2 cm, which are folded into a container to prevent spillage. According to Hansel et al. (1995), water reacts with H_3O^+, producing $H_3O^+ \cdot H_2O$ and therefore causing some loss of H_3O^+. It turned out that when using 20 µl of water, this loss is substantial. Therefore, after the sample is put in the oven, it is kept at 50°C until the water is evaporated, which takes about 20 minutes. After the water is evaporated, the oven program is started. The nitrogen flow through the oven is 50 ml/min. Three replicas are made for the samples with fulvic acid and two for the blanks.
Student's t-test is used to determine which detected ions are attributable to the fulvic acid. The maximum p-value that is used is 0.05.

Results

Table 11 shows that only a small fraction is recovered. Some loss of mass can be explained by fragmentation. After the measurement, the filters contain a distinct stain. This indicates that not all fulvic acid is desorbed. Table 11 also shows that the addition of the salts decreases the recovery. The addition of ammonium nitrate caused the production of large amounts of O_2N^+ (m/z 45.992) during all temperature steps, but the most at 200°C, making this salt less suitable as an addition to the solvent. This sample also caused the H_3O^+ level to increase at the 200°C step at all replicas. The other three samples had a stable H_3O^+ level with a decrease between 5% and 13%, except for three measurements (a blank of the second sample and a fulvic acid measurement of the first and fourth sample) that had a short drop between 21% and 34% at the start of the oven program, for the program was started a little too soon in those cases. Although this is not desirable, the effect of this drop is expected to be very minimal for it lasts less than a minute, and are therefore not excluded from the analysis. Table 11 also shows the number of detected ions that are attributable to the fulvic acid and how many of these ions are not identified. Since in all four cases more than 95% of the ions are identified, the calculation of the elemental composition is reliable.

Table 11. Detected amount of fulvic acid and the number of ions that are attributable to the fulvic acid. It also shows how many of these ions are not identified.

Solvent	µg detected	Number of ions	Not identified
1. Water	2.201	767	26
2. Water + ammonium sulfate	0.803	326	12
3. Water + ammonium nitrate	1.911	499	15
4. Water + ammonium bisulfate	1.750	847	37

Table 12 shows the distribution of the detected mass among the different oven steps. This shows that each time the temperature increases, more is detected during one oven step. There is only one exception to this rule, which is solvent number 3 at 250°C. This trend raises the question how much would be detected at 400°C or even higher temperatures, for this might increase the detected mass a lot.

Table 12. Detected mass (µg) at each oven step.

Solvent	100 °C	150 °C	200 °C	250 °C	300 °C	350 °C
1. Water	0.007	0.033	0.065	0.246	0.771	1.078
2. Water + ammonium sulfate	0.005	0.013	0.032	0.216	0.252	0.286
3. Water + ammonium nitrate	0.047	0.182	0.383	0.159	0.442	0.697
4. Water + ammonium bisulfate	0.001	0.111	0.252	0.453	0.456	0.476

Table 13 shows the elemental composition of the detected ions. The column 'Ref. ' shows the reference values as indicated by the supplier of the fulvic acid. It shows that compared to carbon, less oxygen is recovered, but more hydrogen and nitrogen. The detected N/C ratio is very high, which raises the question which ratio of the original mass is recovered for each element. This is shown in table 14. This table shows that for nitrogen, between roughly 20% and 40% is recovered. Considering that a part of the initial mass is lost due to fragmentation, it is plausible that very few nitrogen is left on the filter, as opposed to the other elements.

Table 13. Elemental composition of the detected ions. 'Ref.' indicates the reference values from the supplier.

	Ref.	1	2	3	4
H/C	97,9	149,3	143,6	142,6	140,3
O/C	60,4	44,6	36,3	44,1	40,5
N/C	1,2	10,6	42,1	15,2	29,9

Table 14. Recovery percentage of each element.

% Recovered	1	2	3	4
C	2.3	0.7	1.8	1.7
H	3.5	1.1	2.6	2.4
O	1.7	0.4	1.3	1.1
N	20.5	26.2	23.2	42.1

Conclusions

Only a small part of the suwannee river fulvic acid standard I is recovered. It is mostly detected at higher temperatures. Adding different salts at a weight ratio of 2:1 does not increase the recovery, but decrease. The O/C ratio is on average 33% lower, but the N/C ratio has increased 9 to 33 times. The weight of the detected nitrogen is relatively close to the original weight of nitrogen that is put on the filter.

General conclusions

The choice of filter material is of influence on the results. In case of the alkanes it appears that quartz filter 'holds' the compound better than aluminium foil. This can be a useful feature when the aim is to prevent a substance from evaporating before the measurement, but it can also be a drawback for a substance might desorb less easy during the measurement. The results of the 33 compounds show that more compounds (16 vs 12) are better recovered from quartz filter, and that more compounds (18 vs 8) are more detected at lower temperatures on aluminium foil.

Longer alkanes are more detected at higher temperatures. This is also the case with the alkanoic acids (compounds 21, 22 and 23).

Part 2 showed that relatively few oxygen is detected. Upon fragmentation, the parts without oxygen tend to get protonated. Part 3 confirms this, for oxygen is the element that is recovered worst. With the fulvic acid, nitrogen is recovered many times better than the other compounds. Part 2 also shows that nitrogen is better recovered than hydrogen and oxygen, but not clear as in part 3.

Future research

It appeared that conclusions are often true for a compound class only and not for all compounds in general. Therefore it is recommended to analyse multiple compounds of the same class to be able to draw more conclusions.
It is also recommended to find a technique to improve the desorption of fulvic acid. Ideas for improvement are other solvents, other filter materials and increase the duration of the oven steps and add higher oven steps to the program.

References

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., ... & Jimenez, J. L. (2008). O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environmental Science & Technology, 42(12),* 4478-4485.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., & Lindinger, W. (1995). Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level. *International Journal of Mass Spectrometry and Ion Processes*, *149*, 609-619.

Holzinger R., Williams J., Herrmann F.,Lelieveld J. & Donahue N. M. (2010). Aerosol analysis using a Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometer (TD-PTR-MS): a new approach to study processing of organic aerosols. *Atmospheric chemistry and physics 10 (5),* 2257-2267

Španěl, P. & Smith, D. (1998). Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and $O_2^+$with several aromatic and aliphatic hydrocarbons. *International Journal of Mass Spectrometry*, *181*(1), 1-10.

Appendix 1: Fragments

Note: the amount of nmol stated after each fragment is not very precise (an error of 10% is possible), but intended as an indication of how often a fragment is detected compared to the other fragments.

	Compound; Solvent	Molecular weight (g/mol)	Fragments (quartz)
1	$C_{18}H_{38}O$ Ethanol	270.49	39.024 C3H2H+ (2.5 nmol); 41.039 C3H4H+ (2.9 nmol); 43.054 C3H6H+ (1.3 nmol); 57.073 C4H8H+ (1.0 nmol); 71.093 C5H10H+ (0.8 nmol) 85.113 C6H12H+ (1.0 nmol) 99.134 C7H14H+ (0.23 nmol) 113.147 C8H16H+ (0.14 nmol)
2	$C_9H_{18}O$ Ethanol	142.24	39.022 C3H2H+ (5 nmol); 41.039 C3H4H+ (9 nmol) 55.054 C4H6H+ (4 nmol); 57.070 C4H8H+ (2 nmol); 69.071 C5H8H+ (10 nmol); 83.085 C6H10H+ (6 nmol); 143.142 complete protonated molecule (4 nmol)
3	$C_8H_5NO_2$ Actone	147.13	102.024 C7H3NH+ (2.2 nmol) 104.048 C7H5NH+ (1.3 nmol) 105.033 C7H4OH+ (1.4 nmol) 130.049 C8H3ONH+ (18 nmol) 148.030 complete (59 nmol)
4	$C_{20}H_{24}N_2O_2$ Water	324.42	203.091 C9H14O5H+
5	$C_2H_5NO_2$ Water	75.07	32.050 CH5NH+ (10 nmol) 61.029 C2H4O2H+ (3.1 nmol) 76.040 complete (3.0 nmol)
6	$C_3H_7NO_2$ Water	89.09	42.034 C2H3NH+ (1.4 nmol); 44.051 C2H5NH+ (1.3 nmol); 60.044 C2H5ONH+ (0.1 nmol) 70.068 (0.4 nmol) C3H3NOH+ ? [2] 72.079 (0.2 nmol) C3H5NOH+ ?
7	$C_3H_7NO_3$ Water	105.09	42.034 C2H3NH+ (2.2 nmol) 44.050 C2H5NH+ (1.6 nmol) 70.075 (1.9 nmol)

[2] A question mark indicates that the fragment was not identified by the computer program, and that the molecule formula is just a sugestion.

8	$C_4H_7NO_4$ Water	133.10	84.045 C4H5ONH+ (0.1 nmol) 98.024 C4H3O2NH+ (0.4 nmol) 99.009 C4H2O3H+ (0.7 nmol) 100.042 C4H5O2NH+ (0.1 nmol) 130.052 (1.7 nmol)	
9	$C_4H_9NO_2$ Water	103.12	84.045 C4H5ONH+ (3 nmol) 86.061 C4H7ONH+ (111 nmol)	
10	$C_4H_9NO_3$ Water	119.12	42.034 C2H3NH+ (0.5 nmol); 43.019 C2H2OH+ (2.2 nmol); 43.052 C3H6H+ (0.3 nmol); 44.014 CHONH+ (0.5 nmol) 44.050 C2H5NH+ (0.6 nmol) 45.034 C2H4OH+ (49 nmol) 46.028 CH3ONH+ (0.4 nmol) 47.013 CH2O2H+ (1.8 nmol) 56.049 C3H5NH+ (1.5 nmol) 56.057 (1.1 nmol) 57.033 C3H4OH+ (0.2 nmol) 57.042 (0.3 nmol) 58.031 C2H3ONH+ (0.1 nmol) 58.065 C3H7NH+ (2 nmol); 59.011 C2H2O2H+ (0.04 nmol) 59.049 C3H6OH+ (0.5 nmol) 60.045 C2H5ONH+ (0.1 nmol) 60.081 C3H9NH+ (0.1 nmol) 61.028 C2H4O2H+ (3 nmol); 98.095 (2.9 nmol); 112.073 (1.9 nmol)	
11	$C_5H_{11}NO_2S$ Water	149.21	49.012 CSH4H+ ?	
12	$C_5H_9NO_4$ Water	147.13	84.052 C4H5ONH+ (2.3 nmol) 86.060 C4H7ONH+ (0.9 nmol) 130.057 (0.3 nmol)	
13	$C_6H_{13}NO_2$ Water	131.17	44.050 C2H5NH+ (1.3 nmol); 86.095 C5H11NH+ (5.1 nmol); 132.092 complete (2.2 nmol)	
14	$C_6H_{13}NO_2$ Water	131.17	Quartz: 44.050 C2H5NH+ (0.6 nmol); 86.101 C5H11NH+ (0.8 nmol); 132.100 complete (0.02 nmol) 154.158 C10H19NH+ (0.3 nmol) 200.161 C11H21O2NH+ (2.0 nmol) 210.151 C12H19O2NH+ (1.4 nmol) 227.178 C12H22O2N2H+ (1.2 nmol)	Alu: 1.8 nmol 6.7 1.6 0.8 1.5 0.008 0.001
15	$C_7H_7NO_2$ Water	137.14	94.065 C6H7NH+ (9 nmol); 120.045 C7H5ONH+ (11 nmol); 138.054 complete (39 nmol)	

16	$C_9H_{11}NO_2$ Water	165.19	44.049 C2H5NH+ (0.4 nmol) 86.105 C3H3O2NH+ (1.7 nmol) 91.057 C7H6H+ (0.9 nmol) 232.108 C10H17O5NH+ (0.4 nmol) 234.142 C10H19O5NH+ (0.6 nmol) 278.124 C11H19O7NH+ (0.9 nmol)
17	$C_9H_{11}NO_3$ Water + formic acid (1:50)	181.19	95.048 C6H6OH+ (0.027 nmol) 107.064 (0.034 nmol) 109.065 C7H8OH+(0.027 nmol) 121.064 C8H8OH+ (0.018 nmol)
18	$C_{11}H_{12}N_2O_2$ Water	204.23	118.073 C8H7NH+ (5.4 nmol) 132.086 C9H9NH+ (1.4 nmol)
19	$C_5H_6O_3$ Water	114.10	43.018 C2H2OH+ (22 nmol); 45.035 (C2H4OH+) (11 nmol); 87.044 C4H6O2H+ (32 nmol); 115.039 complete (9 nmol)
20	$C_6H_{10}O_5$ Water	162.14	31.019 CH2OH+ (0.8 nmol) 39.023 C3H2H+ (0.6 nmol) 41.040 C3H4H+ (0.5 nmol) 43.018 C2H2OH+ (1.1 nmol) 45.034 C2H4OH+ (0.8 nmol) 53.038 C4H4H+ (0.2 nmol) 57.036 C3H4OH+ (0.4 nmol) 69.033 C4H4OH+ (2.9 nmol) 73.028 C3H4O2H+ (0.2 nmol) 81.034 C5H4OH+ (0.5 nmol) 85.028 C4H4O2H+ (6.1 nmol) 97.026 C5H4O2H+ (1.6 nmol) 99.044 C5H6O2H+ (0.2 nmol) 109.028 C6H4O2H+ (0.4 nmol) 127.039 C6H6O3H+ (0.9 nmol) 145.064 C6H8O4H+ (0.7 nmol) 163.058 complete (0.2 nmol)
21	$C_{10}H_{20}O_2$ Ethanol	172.26	41.038 C3H4H+ (1.0 nmol) 43.057 C3H6H+ (1.2 nmol) 57.074 C4H8H+ (1.3 nmol) 71.089 C5H10H+ (1.1 nmol) 81.070 C6H8H+ (0.8 nmol) 85.108 C6H12H+ (0.7 nmol) 95.093 C7H10H+ (1.3 nmol) 155.148 C10H18OH+ (0.9 nmol) 173.144 complete (36 nmol)

22	$C_{15}H_{30}O_2$ Ethanol	242.40	41.039 C3H4H+ (0.3 nmol) 43.055 C3H6H+ (0.2 nmol) 57.079 C4H8H+ (0.6 nmol) 71.097 C5H10H+ (0.7 nmol) 81.070 C6H8H+ (0.2 nmol) 85.106 C6H12H+ (0.6 nmol) 95.089 C7H10H+ (0.2 nmol) 225.220 C15H28OH+ (0.4 nmol) 243.230 complete (36 nmol)
23	$C_{18}H_{36}O_2$ Ethanol	284.48	243.229 C15H30O2H+ (3 nmol); 285.273 complete (24 nmol)
24	$C_5H_8O_4$ Water	132.11	43.019 C2H2OH+ (17 nmol); 45.035 C2H4OH+ (8 nmol); 87.043 C4H6O2H+ (27 nmol); 115.038 C5H6O3H+ (7 nmol)
25	$C_6H_{10}O_4$ Ethanol	146.14	39.023 C3H2H+ (1.3 nmol) 43.019 C2H2OH+ (1.8 nmol) 55.054 C4H6H+ (4 nmol) 83.050 C5H6OH+ (3.4 nmol) 85.059 C5H8OH+ (4.3 nmol) 101.049 C5H8O2H+(6 nmol) 111.032 C6H6O2H+? (3.1 nmol) 129.033 C9H4OH+ (5.1 nmol) 285.281 C18H36O2H+ ? / C17H32O3H+ ?
26	$C_{24}H_{38}O_4$ Ethanol	390.56	41.040 C3H4H+ (0.4 nmol) 45.034 C2H4OH+ (0.8 nmol) 57.035 C3H4OH+ (0.5 nmol) 57.070 C4H8H+ (0.5 nmol) 149.028 C8H4O3H+ (5 nmol) 279.193 C17H26O3H+ (0.4 nmol) 391.271 complete (3.7 nmol)
27	$C_{12}H_9N$ Acetone	167.21	168.071 Complete
28	$C_{16}H_{10}$ Ethanol	202.25	203.082 complete
29	$C_{16}H_{10}$ Ethanol	202.25	203.094 complete
30	$C_{14}H_{10}O$ Acetone	194.23	195.079 complete (33 nmol) 209.060 (19 nmol)
31	$C_{14}H_{10}O_4$ Ethanol	242.23	45.000 (0.3 nmol) 77.039 C6H4H+ (2.6 nmol) 79.055 C6H6H+ (7.5 nmol) 95.049 C6H6OH+ (1.3 nmol) 105.033 C7H4OH+ (14 nmol) 123.042 C7H6O2H+ (45 nmol)
32	$C_6H_5NO_2$ Water	123.11	106.033 C6H3ONH+ (1 nmol); 124.039 complete (14 nmol)

33	CH_4O_3S Water	96.11	-