Analytical method development for the analysis of polar organic compounds in sea spray particles and the oceans surface microlayer

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FILGAS

Introduction

More than 70% of the Earth's surface is covered by ocean. Under special meteorological conditions (e.g. wind speed lower than 4 m s^{-1}) a thin film can be formed which is enriched in inorganic and organic matter. This layer is only a few micro meter thick but the presence of such an organic film at the water surface has several physical chemical effects. For example, the layer can function as a barrier for transport processes of the air - water interface. Such layer can influence climate because the water evaporation or the sea salt formation capacity of the ocean can be limited. Additionally, such barrier prevents the uptake of soluble compounds such as CO_2 into the ocean.

To understand the role of such surface film in the ocean-atmosphere interaction and the climate system, it is necessary to have better insights into the chemical composition of the organic ocean microlayer.

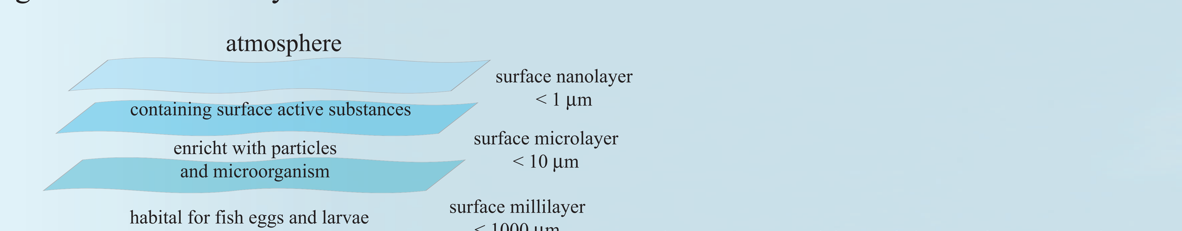

Fig. 1. Composition of the surface microlayer according Hardy and Word (1986) and Donaldson et al. (2006).

FILGAS project

The ocean surface layer samples will be taken in the Baltic Sea. This site offers very complex hydrographical conditions (T, salinity) with a permanent strong stratification and brackish water. The salinity is 15-25 PSU (practical salinity unit; 1 PSU = 1 kg salt per 1000 kg water) and the pH value lies between 8.0 – 8.5. The project is part of the pact project (FILGA, film and gas exchange) with the Baltic Sea Research Institute Warnemünde (IOW) and the University of Kiel. Aim of the project is to characterise the function and formation of the film at the interface of ocean – atmosphere and the production and transport processes of trace gases.

Fig. 2. Sampling site in Baltic Sea

Fig. 3. Sampling method - the „Skimmer" a rotating drum

Method Development

Our part in the FILGAS project is the analysis of the polar organic compound composition in the ocean surface microlayer. To iedntify the organic compounds in the ocean surface film, samples from the Baltic Sea will be analysed with different hyphnated techniques such as CE/ESI-MS, GC/MS and HPLC/MS. Main target classes are amino acids, carboxylic acids, fatty acids, carbohydrates, aldehydes/ketones, phenolic compounds. In this work, we present the outcome from the development of the analytical methods and analytical figures of merits for each methods

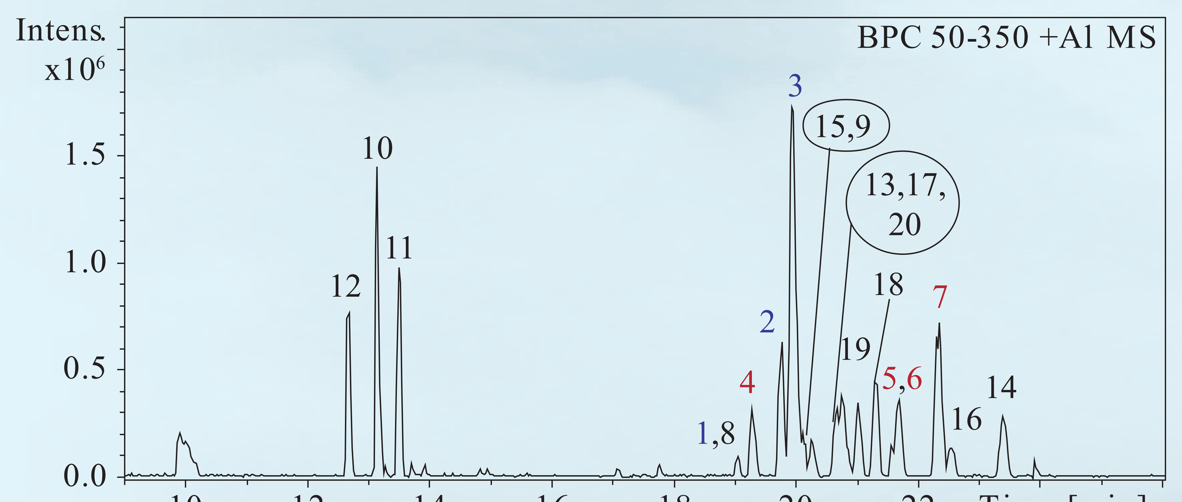

Fig. 4. The base peak chromatogram (m/z 50 - 350) of 20 proteinogenic amino acids. Standard Solution with a concentration of 150 µM.

Aliphatic amino acids
1 Alanine
2 Isoleucine
3 Leucine
4 Valine

Aromatic amino acids
5 Phenylalanine
6 Tryptophan
7 Tyrosine

Polar amino acids
8 Serine
9 Threonine
10 Arginine
11 Histidine
12 Lysine
13 Proline
14 Prolin OH
15 Asparagine
16 Aspartic acid
17 Glutamine
18 Glutamic acid
19 Cysteine (dimer)
20 Methionine

For the analysis of 20 proteinogenic amino acids we use capillary electrophoresis coupled to electrospray ionisation ion trap mass spectrometry (CE/ES-ITMS). The method is based on the conditions presented by Soga et al. (2004) though we have modified various parameters to fit to our purposes. Separations were carried out on a fused silica capillary column with ID 50 µm and OD 360 µm and a total length of 100 cm (Chromatographie Service GmbH). The used buffer was a 1.1 M formic acid solution with a pH 2.3 and the separation voltage was 30 kV. To generate a stable electrospray a sheath liquid of 1:1 iso-propanol : water was used. The evaluation of the method was performed in the concentration range between 5-150 µM (150, 100, 75, 50, 25, 15, 5 µM).

With the same technique we developed a method for the carboxylic acids separation. Separations were carried out on a fused silica capillary column with ID 50 µm and OD 360 µm and a total length of 70 cm (Chromatographie Service GmbH). The used buffer system was a 20 mM ammonium acetate and 30 mM ammonium hydroxide pH 9.9 and used the separation voltage was 20 kV. To generate a stable electrospray a sheath liquid of 1:1 iso-propanol : water was also used. The evaluation of the method was performed in the concentration range between 5-100 µM (100, 75, 50, 25, 10, 5 µM).

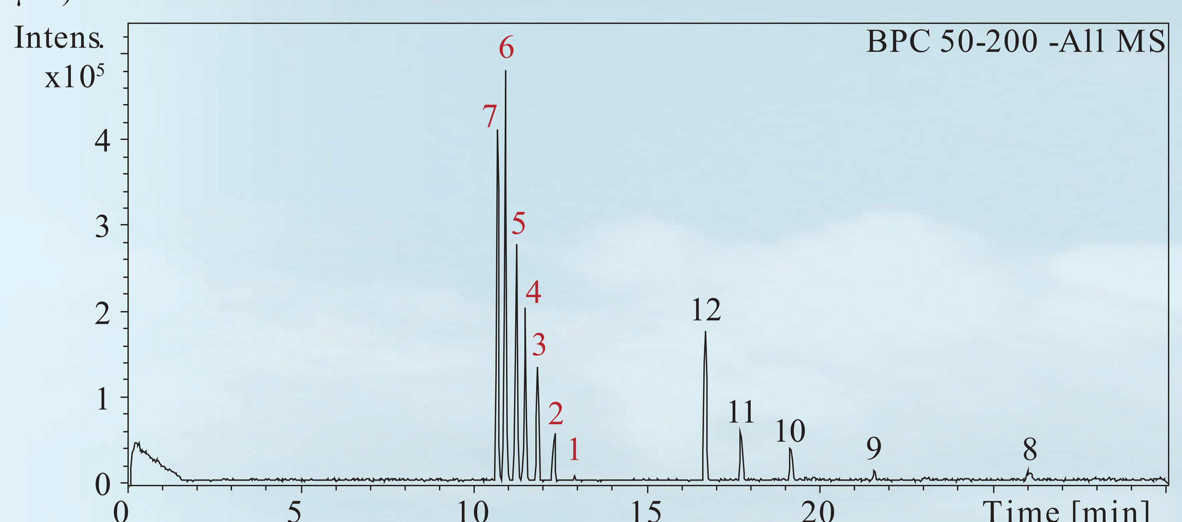

Fig. 5. The base peak chromatogram (m/z 50-20) of mono and dicarboxylic acids. Standard solution with a concentration of 100 µM.

Mono carboxylic acids
1 Butyric acid
2 Valeric acid
3 Hexanoic acid
4 Heptanois acid
5 Oxo octanoic acid
6 Nonanoic acid
7 Decanoic acid

Dicarboxylic acids
8 Butandioic acid
9 Pentandioic acid
10 Hexandioic acid
11 Heptandioic acid
12 Octandioic acid

For the analysis of carbohydrates in the microlayer, we have developed a method using derivatisation GC/MS technique based on the method presented by Medeiros and Simoneit (2007). This method silylates the OH groups in the carbohydrates so that they can be analysed using GC/MS. The capillary column used was a HP-5MS with an ID 0.25 mm and a total length of 30m. The injector temperature was 260 °C. The column temperature program is as follows: 85 °C for 1 min then 5 °C min^{-1} increase to 180 °C. Hold at 180 °C for 5 min and then 7 °C min^{-1} increase to 280 °C and hold for 2 min. To clean the column, the temperature was raised to 310 °C and kept for 10 min. The evaluation of the method was performed in the concentration range between 5-50 µM

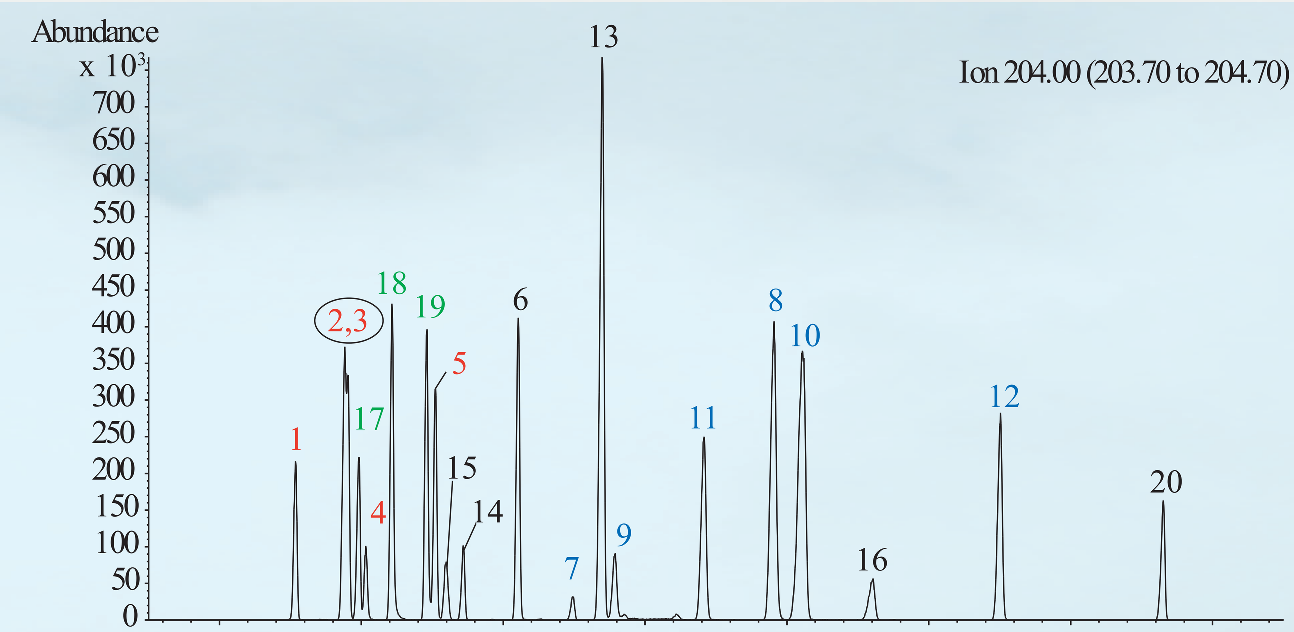

Fig. 6. Extracted ion chromatogram of ion 204 from a succharide standard solution with a concentration of 50 µM.

Aldopentose
1 Arabinose 1
2 Arabinose 2
3 Ribose 1
4 Ribose 2
5 Xylose 1
6 Xylose 2

Aldohexose
7 Mannose 1
8 Mannose 2
9 Galactose 1
10 Galactose 2
11 Glucose 1
12 Glucose 2

Ketohexose
13 Fructose

Dialcohol
14 Arabitol
15 Xylitol
16 Mannitol

Biomass burn tracer
17 Anhydrogalactopyranose
18 Anhydromannosepyranose
19 Anhydroglucopyranose

Internal standard
20 myo-Inositol

Table 1. Results of the amino acid method evaluation with retention times, correlation coefficients and detection limits.

amino acids L-form	retention time [min]	correlation coefficient	detection limit [µmol l⁻¹]
Alanine	16.2 ± 0.4	1.000	7.0 ± 1.8
Isoleucine	17.7 ± 0.4	0.999	3.0 ± 0.9
Leucine	17.9 ± 0.4	0.999	3.0 ± 0.8
Valine	18.2 ± 0.5	1.000	2.4 ± 0.7
Phenylalanine	19.3 ± 0.4	0.999	1.2 ± 0.5
Tryptophan	20.3 ± 0.7	1.000	18.1 ± 9.2
Tyrosine	21 ± 0.7	1.000	1.6 ± 0.5
Serine	18.0 ± 0.5	0.998	5.0 ± 1.4
Threonine	19.1 ± 0.6	1.000	5.3 ± 2.3
Arginine	12.6 ± 0.3	1.000	2.6 ± 0.8
Histidine	13 ± 0.3	0.999	1.2 ± 0.5
Lysine	12.2 ± 0.2	0.999	3.7 ± 1.6
Proline	19.5 ± 0.6	1.000	42.1 ± 7.8
Proline OH	21.9 ± 0.7	0.999	25.8 ± 11.4
Asparagine	18.9 ± 0.6	0.999	4.8 ± 2.8
Aspartic acid	21.0 ± 0.7	0.999	5.4 ± 2.4
Glutamine	20.0 ± 0.6	0.999	9.8 ± 3.8
Glutamic acid	20.0 ± 0.6	0.999	2.7 ± 1.0
Cysteine (Dimer)	19.7 ± 0.6	0.999	7.3 ± 2.8
Methionine	19.5 ± 0.6	0.999	1.3 ± 0.4

Table 3. Results of the sugar method evaluation with retention times, correlation coefficients and detection limits.

sugars	retention time [min]	correlation coefficient	detection limit [µmol l⁻¹]
DL-Arabinose 1	17.03 ± 0.02	1.000	2.5 ± 0.1
DL-Arabinose 2	17.72 ± 0.02	1.000	1.2 ± 0.4
D-(+)-Ribose 1	17.76 ± 0.02	0.997	2.1 ± 0.4
D-(+)-Ribose 2	18.02 ± 0.02	0.998	2.8 ± 0.4
D-(+)-Xylose 1	19.00 ± 0.02	0.999	0.7 ± 0.2
D-(+)-Xylose 2	20.16 ± 0.02	0.999	3.1 ± 1.0
D-(+)-Mannose 1	20.93 ± 0.02	0.999	5.2 ± 0.8
D-(+)-Mannose 2	23.73 ± 0.02	0.999	1.8 ± 0.1
D-(+)-Galactose 1	21.52 ± 0.02	0.999	3.0 ± 0.6
D-(+)-Galactose 2	24.14 ± 0.03	0.999	1.5 ± 0.6
D-(+)-Glucose 1	22.76 ± 0.03	0.999	2.3 ± 0.4
D-(+)-Glucose 2	26.94 ± 0.02	0.999	3.5 ± 1.3
D-(-)-Fructose	21.34 ± 0.02	1.000	1.3 ± 0.7
D-(+)-Arabitol	19.39 ± 0.02	1.000	2.1 ± 0.4
Xylitol	19.14 ± 0.02	1.000	2.1 ± 1.3
D-Mannitol	25.12 ± 0.03	1.000	3.8 ± 0.6
1,6-Anhydro-β-D-galactopyranose	17.90 ± 0.02	1.000	1.6 ± 0.8
1,6-Anhydro-β-D-mannosepyranose	18.37 ± 0.02	1.000	2.7 ± 0.6
1,6-Anhydro-β-D-glucopyranose	18.86 ± 0.02	1.000	1.9 ± 0.7

The following tables list the analytical figures of merits (retention times, correlation coefficients and the detection limits) from the analysis of the standard compounds of the amino acids (Table 1), the carboxylic acids (Table 2) and sugar (Table 3).

Table 2. Results of the carboxylic acid method evaluation with retention times, correlation coefficients and detection limits.

carboxylic acids	retention time [min]	correlation coefficient	detection limit [µmol l⁻¹]
Butyric acid	13.5 ± 0.8	0.995	14.2 ± 3.7
Valeric acid	12.9 ± 0.7	1.000	2.8 ± 1.1
Hexanoic acid	12.3 ± 0.6	0.999	3.8 ± 1.4
Heptanois acid	11.9 ± 0.9	0.999	2.8 ± 1.0
Oxo octanoic acid	11.3 ± 0.5	1.000	1.7 ± 0.7
Nonanoic acid	11.2 ± 5.6	1.000	2.4 ± 1.3
Decanoic acid	11.1 ± 0.5	0.998	2.7 ± 1.1
Butandioic acid	26.5 ± 4.8	1.000	11.6 ± 3.9
Pentandioic acid	23.6 ± 2.3	0.999	15.4 ± 6.3
Hexandioic acid	20.7 ± 0.7	1.000	5.9 ± 1.1
Heptandioic acid	19.0 ± 1.5	0.999	5.4 ± 1.5
Octandioic acid	11.8 ± 1.3	1.000	4.9 ± 1.5

Summary and Outlook

We have developed and evaluated the methods for the analysis of amino acids, carboxylic acids and sugars using CE/ESI-ITMS and GC/MS. These methods will be use to analyse ocean surface microlayer and sea spray aerosol samples from the Baltic Sea. The obtained results will improve our understanding of the film composition and furthermore help to get information for its role, for example, for gas exchange processes.

References

Donaldson, D.J. and Vaida, V., 2006. The influence of organic films at the air-aqueous boundary on atmospheric processes. Chemical Reviews, 106(4): 1445-1461.

Hardy, J. and Word, J., 1986. Contamination ot the water surface of puget sound. Puget Sound Notes: 3.

Medeiros, P.M. and Simoneit, B.R.T., 2007. Analysis of sugars in environmental samples by gas chromatography-mass spectrometry. Journal of Chromatography A, 1141(2): 271-278.

Soga, T., Kakazu, Y., Robert, M., Tomita, M. and Nishioka, T., 2004. Qualitative and quantitative analysis of amino acids by capillary electrophoresis-electrospray ionization-tandem mass spectrometry. Electrophoresis, 25(13): 1964-1972.

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