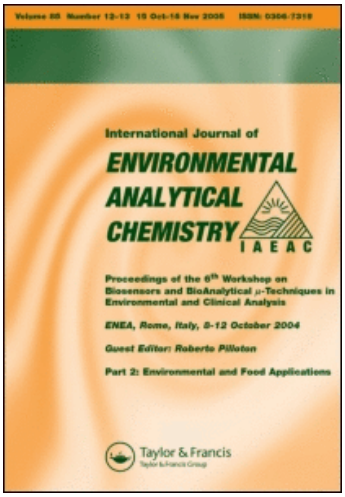

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Andreas Limbeck[a]; Hans Puxbaum[a]
[a] Institute for Analytical Chemistry, Vienna University of Technology, Vienna, Austria

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A GC-MS METHOD FOR THE DETERMINATION OF POLAR ORGANIC COMPOUNDS IN ATMOSPHERIC SAMPLES

ANDREAS LIMBECK and HANS PUXBAUM*

Institute for Analytical Chemistry, Vienna University of Technology, Getreidemarkt 9/1514, A-1060 Vienna, Austria

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A new method was developed for the simultaneous determination of polar organic compounds from liquid samples (atmospheric hydrometeors) as well as for aerosol samples. The analysis of aerosol samples includes a new extraction method using diethylether, methanol and organic free water to obtain a liquid sample solution. The sample-separation into two classes of organic compounds with different polarity was performed using solid phase extraction (SPE). The adsorbed fraction contains weakly polar compounds like monocarboxylic acids (C8 – C18), alcohols (C8 – C18), phthalates, aliphatic and aromatic aldehydes. The solution passing the SPE-tube contains the not adsorbed strong polar organic compounds like dicarboxylic acids (C2 – C9) and related compounds. After a sample pretreatment of the two fractions, including esterification of the acids and extraction with cyclohexane, the samples were analyzed with GC-MS. Recoveries for the determined compounds ranged from 60 – 100%, the experiments have shown that substances with longer carbon chains exhibit decreased recoveries. The reproducibility given as the relative standard deviation varies from 5 – 15%. The absolute amount of an individual compound which is necessary for detection is about 10 to 50 ng. For quantification the absolute amounts varies in a range of 25 to 150 ng. The new method is applied for the analysis of aerosol and cloud water samples from a continental background site in Central Europe (Sonnblick Observatory).

Keywords: Monocarboxylic acids; dicarboxylic acids; weakly polar organic compounds; aerosol; cloud water; solid phase extraction; GC-MS

INTRODUCTION

Different groups of polar organic compounds have been determined in atmospheric samples with different methods of sample preparation and analysis. In this respect, weakly polar organic compounds (WPOC's), namely phthalates, phenols, esters and aldehydes, have been extracted from aerosol samples with organic solvents (e.g. benzene and methylenechloride) and subjected to

* Corresponding author. Fax: +43-1-58801-15199. E-mail: hpuxbaum@mail.zserv.tuwien.ac.at

GC-MS[1,2]. With this extraction method weakly polar compounds are separated with high yields, but highly polar compounds could not be determined. For the analysis of dicarboxylic acids (DCA's, in the range from 2 to 10 carbon atoms) and monocarboxylic acids (MCA's, in the range from C8 to C26) aerosol samples have been extracted with aqueous solutions [3] or with organic solvents like methanol, isopropanol or methylenechloride [4,5]. After extraction of the samples, evaporation of the solvent and further derivatization of the residue (esterification) the analytes were usually determined by GC-MS. With these methods highly polar compounds are amenable to analysis. Unfortunately, this is not the case for volatile compounds like alcohols or aldehydes. Summing up it is not possible to obtain the whole information about polar organic compounds (WPOC's, MCA's and DCA's) from one single sample preparation scheme.

For the analysis of liquid samples (e.g. snow, rain or cloud water) similar methods of extraction and derivatisation were used as for aerosols. A common method is liquid/liquid extraction combined with various organic solvents as extractants like isopropanol, n-hexane, benzene or methylenechloride coupled with GC-MS analysis [6]. With this method only WPOC's could be separated with high yields, highly polar compounds with good water solubility like DCA's are not accessible for analysis. With liquid/liquid extraction MCA's are available in a range from C6 to C30 [7,8], but large sample volumes (about 1.0 to 2.0 L) were needed for preconcentration. Compounds with low volatility like DCA's or MCA's with a chain length of 14 or more carbon atoms could be determined by a method reported by Kawamura and Yasui[9] based on the esterification of the preconcentrated aqueous solution and analysis via GC-MS. A method for the determination of volatile organic acids (C1 to C9) in rain samples is described by Kawamura and Kaplan [10]. The acids were converted into the p-bromophenacyl esters and analyzed via capillary gas chromatography. However, these methods do not allow the analysis of MCA's in the range from C10 to C14 and of some WPOC (e.g. benzaldehyde, 1-octanol or nonanal), because of their volatility and their poor solubility in organic solvents.

Here we describe a new method for the separation of different classes of oxygenated compounds (MCA's, DCA's, aldehydes, alcohols,...) from one sample by solid phase extraction (SPE). The method is applicable for liquid as well as for aerosol samples. The analysis of aerosol samples includes a new extraction method. SPE was used to separate the sample into two fractions. The adsorbed fraction, containing MCA's, alcohols, phthalates, aliphatic and aromatic aldehydes, and the fraction passing the SPE-tube, containing DCA's and related compounds. The adsorbed compounds were eluted from the SPE-cartridge with methanol. The MCA's were converted into the corresponding methyl-esters and the aldehydes into the dimethylacetals. These products and the compounds which

did not react with the esterification reagent like alcohols or phthalates were extracted with cyclohexane and analyzed by GC-MS. From the second separated fraction, containing DCA's, aromatic acids and other polyfunctional compounds, the propyl-esters were formed, extracted with cyclohexane and analyzed by GC-MS.

The new method is applied to the analysis of polar organic compounds in cloud water and aerosol samples from a continental background site in Central Europe (Sonnblick Observatory, 3106 m a.s.l.).

EXPERIMENTAL

Chemicals and reagents

Solvents of p.a. grade purity (methanol, propanol and cyclohexane) and the esterification reagents with puriss. quality were purchased from Merck and Fluka Chemical Corp., respectively. All standards were from Fluka Chemical Corp. or from Merck with the highest available purity. The organic free pure water was from a Millipore® ultra pure water system (Milli Q-plus 185) fed with distilled water.

Standard stock solutions (1 mg/mL) from the different compound classes (e.g. alcohols, MCA's, ...) were prepared by dissolving the corresponding substances in methanol. 2-Bromo-dodecanoic acid (used as internal standard) was dissolved in propanol, and the 12-bromo-1-dodecanol solution was made with methanol. Low concentration mixed standard solutions and the internal standards were made from these stock solutions by further dilution with water. These standards were prepared daily. All standard stock solutions were stored at 4°C.

All synthetic sample solutions were prepared as follows. Well known amounts of standard compounds (aliphatic alcohols, aliphatic and aromatic aldehydes, aliphatic monocarboxylic acids, aliphatic and aromatic dicarboxylic acids and some esters) were added to a few mL of organic free water into a graduated measuring flask. Before the sample was filled up with water to a total volume of 25 mL, a defined amount of methanol (1 mL) was added to achieve a final concentration of 4% methanol in the aqueous solution. Blank solutions were made with 1 mL methanol and 24 mL organic free water.

Samples

Aerosol and cloud water samples were collected in April and May 1997 at the Sonnblick Observatory (SBO), which is located on the top of the Mount Son-

nblick in the Austrian Alps (12°57′ E; 47°03′ N). The SBO is a continental background station since no local pollution sources are nearby. The cloud water samples were collected with a newly designed cloud-water-sampling device (CWS) which is an active collector for hydrometeors. The interstitial aerosol samples were collected downstream the CWS via a manifold using 47 mm Quartz fiber filter (Pallflex TISSUQUARTZ 2500QAT-UP) [11]. To exclude any contamination from the sampling procedure itself, field blanks were also collected. After sampling the filters were stored in petri-dishes with a parafilm cap in the refrigerator at 4°C. The cloud water samples were kept frozen in polyethylene bags until analysis.

Sample pretreatment

Aerosol samples

The filters were extracted at room temperature using ultrasonic shaking for 15 minutes with 3 mL diethylether. The extract was filled into a 25 mL measuring flask and dried carefully with a nitrogen blow down system at room temperature. The wet filter was dried at room temperature in a nitrogen stream. To obtain the highly polar compounds like DCA's another extraction step was necessary. Therefore, 1 mL methanol and 2 mL organic free water were added and the filter was extracted for another 15 minutes in the ultrasonic bath. The extract was combined with the residue from the ether extraction. In a third extraction step this procedure was repeated with 3 ml organic free water. After the extraction the filter was rinsed with water. The extract from the third extraction step was added to the graduated measuring flask. For the separation into the different classes of compounds via SPE it was necessary to dilute the extraction solution with pure water to a total volume of 25 mL in order to achieve a total concentration of 4% methanol in the sample solution. This constant amount of 4% methanol is necessary for the quantitative separation with SPE into fractions with different polarity.

Cloud water samples

The cloud water samples were melted at room temperature in the closed polyethylene bag. A total volume of 50 mL was filled into a graduated measuring flask. To obtain the optimal conditions for the SPE 2 mL methanol were added to the solution, to achieve a total concentration of approximately 4% methanol as for the aerosol samples.

Solid-phase-extraction and derivatisation (Figure 1)

The sample-separation into different classes of organic compounds was performed using a C-18 cartridge [IST, 221–0020-H].This type of SPE-columns are packed with 200 mg of end capped C18-sorbent. Before the C-18 cartridge could be used a pretreatment was necessary. Therefore, 3 mL of organic free water, followed by 3 ml of methanol were sucked through the sorbent material. The preparation of the SPE-cartridge was finished by purging with another 3 mL of organic free water. After this conditioning step the aqueous sample solution was sucked through the SPE-tube with a flow of 2–3 mL/min.

The aqueous solution passing the SPE-cartridge containing the not adsorbed DCA's and related polar compounds was collected in a 100 mL vacuum flask. This solution was filled successively into a 20 mL measuring flask, and evaporated carefully to dryness in a nitrogen stream at 90°C. The residue was dissolved in 1 mL 1-propanol and treated with 100 µL BF_3-propanol-complex. This solution was spiked with 2-bromo-dodecanoic acid as internal standard (50 µL of a solution of 100 ng/µL concentration). To obtain the propyl-esters the solution was mixed with a stirring apparatus and heated to 95°C for 30 minutes. After the addition of a saturated aqueous solution of NaCl to the cold sample to a total volume of 20 mL the DCA-esters were extracted with 200 µL cyclohexane. This cyclohexane solution was analyzed by GC-MS. The formation of the propylesters was necessary for the determination of oxalic acid. Shorter esters like those obtained with other methods (e.g. esterification with diazomethane) will decompose by the subsequent dilution with saturated NaCl solution.

The SPE-cartridge containing the adsorbed compounds was purged with air for 30 seconds to remove traces of water. From the dried SPE tube the MCA's and the other weakly polar compounds were eluted with 2 × 1.25 mL pure methanol into a 10 ml measuring flask. To this solution 50 µL 12-bromo-1-dodecanol with a concentration of 500 ng/µL were added as an internal standard. To convert the MCA's and aldehydes to the analogous methyl-esters and dimethyl-acetals this solution was treated with 100 µL BF_3-methanol-complex and heated to 60°C for 30 minutes under continuous stirring. The cold solution was diluted with a saturated aqueous solution of NaCl to a total volume of 10 mL. From this solution the MCA-esters and the other WPOC's were extracted with 200 µL cyclohexane. This extract was analyzed by GC-MS.

GC-MS analysis

A HP® 5890 Series II GC was equipped with a capillary column (HP® INNOWax 19091N-133, 30 m, 0.25 mm ID, 0.25 µm film thickness) and a mass

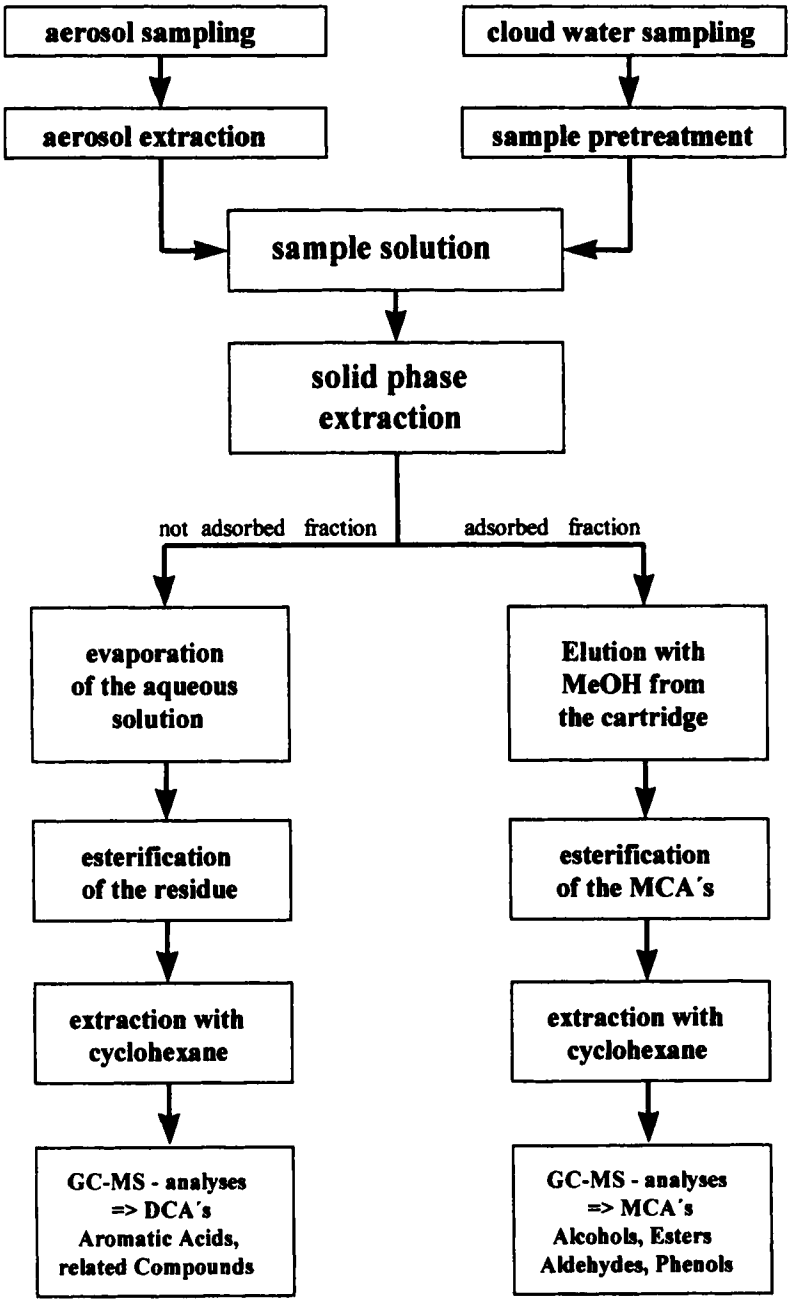

FIGURE 1 Sample separation scheme

selective detector (HP®5971 A). He 5.0 was used as carrier gas. The sample injection was performed with a split/splitless injector at 230°C with an injection volume of 1 µL and a split ratio of 1:50. The MS transferline was kept at 280°C. With this system a total ion chromatogram (TIC) was obtained from each sample. The MSD data was used for peak identification from full mass spectra (45–300 amu) and for quantification. Therefore, the use of an internal standard was necessary to calculate the amounts of these substances from the MS total ion current chromatograms.

Compounds identification and quantification

Identification of compounds and derivatives was performed by comparison of the mass spectra with a spectra library (Wiley), and for available reference standards by comparison of the GC retention times. A compound was positively identified, when the library could name the compound with a quality factor over 80% and the retention time was confirmed with that of the reference standard. If the quality factor was over 80% but there was no reference standard available to check the retention time, the compound was only tentatively identified. Together with the information from the retention time, the length of the carbon chain could be estimated.

The quantification was based on a calibration-function for the complete procedure, which has been determined with standard solutions and the internal standards. For the calculation of the absolute amount of an individual compound the corresponding field blank has been taken into account.

RESULTS

Analytical method

Recoveries and reproducibilities

Synthetic sample solutions containing aliphatic alcohols, aliphatic and aromatic aldehydes, aliphatic monocarboxylic acids, aliphatic and aromatic dicarboxylic acids and some esters at a concentration level of 10 µg/L for each compound were analyzed as described above. The recoveries were calculated from parallel determinations with the same absolute amounts of substances dissolved in methanol. Some compounds could directly be analyzed from these solutions with the GC-MS system (e.g. alcohols or phthalates), for all acids and aldehydes it was necessary to convert them into the corresponding esters and acetals and extract

them with cyclohexane before analysis. The recoveries and reproducibilities for each class of compounds are given in Table I. These values are averages from 4 synthetic samples. Each sample was analyzed two times with the GC-MS system. The recoveries ranged from 60 to 100%, the reproducibility given as the coefficient of variance was in a range from 5 to 15%. The experiments have shown that recoveries and reproducibilities depend on the length of the carbon chain. Substances with longer carbon chains exhibit decreased recoveries and reproducibilities. Another important result of the experiments with synthetic sample solutions was that the determined statistical functions do not depend on the sample volume. For different sample volumes in a range of at least 10 to 100 mL containing the same absolute amount of substance the same results were obtained.

TABLE I Reproducibilities (given as the coefficient of variance), recoveries and quantification limits (LOQ) for different classes of polar organic compounds

Substance	*coefficient of variance*	*recovery*	*limit of quantification*	
			abs. amount	*sample volume**
Monocarboxylic Acids	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Octanoic acid	7.3	105	29	0.6
Decanoic acid	5.8	105	30	0.6
Dodecanoic acid	9.5	104	26	0.5
Tetradecanoic acid	4.9	94	78	1.6
Hexadecanoic acid	5.6	84	107	2.1
Octadecanoic acid	7.8	70	68	1.4
Octadecenoic acid	10.6	74	132	2.6
Alcohols	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Octanol	8.5	98	35	0.7
Dodecanol	5.9	89	29	0.6
Tetradecanol	6.7	75	61	1.2
Hexadecanol	5.0	66	127	2.5
Octadecanol	8.0	61	159	3.2
Aldehydes	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Nonanal	7.7	75	54	1.1
Decanal	5.0	91	18	0.4

Substance	*coefficient of variance*	*recovery*	*limit of quantification*	
			abs. amount	*sample volume**
Dodecanal	5.5	64	20	0.4
Aromatic Compounds	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Diethylphthalate	7.0	107	128	2.6
Dibutylphthalate	6.0	104	35	0.7
2,6-Diisobutyl-phenol	6.9	89	18	0.4
Benzoic acid	9.3	87	81	1.6
Phthalic acid	14.3	59	42	0.8
Dicarboxylic Acids	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Oxalic acid	6.8	89	156	3.1
Malonic acid	8.2	85	18	0.4
Succinic acid	5.2	82	52	1.0
Adipic acid	6.3	74	49	1.0
Ketoacids	[%]	[%]	**ng abs.**	**ng/ml or ng/m^3**
Glyoxylic acid	10.2	-	97	1.9
Pyruvic acid	13.8	-	62	1.2

sample volume*: quantification limits calculated for 50 ml liquid sample or 50 m^3 air sample.

Blanks

To obtain the blank values originating from the analytical method 10 blank solutions (organic free water containing 4% methanol) were analyzed as described above. For some individual compounds blanks could be observed, for example all even numbered MCA's and DCA's and some phthalates. For some compounds the source of the blanks could be given e.g. the MCA's appear to result from the esterification reagents. All other observed compounds must originate from the SPE-cartridge or the used chemicals (e.g. diethylether, methanol and cyclohexane).

Fresh filters and the polyethylene bags were tested for their blanks prior to their use in the field campaigns. Generally, they were found to be free of organic compounds of interest.

Limit of detection and quantification

The LOQ is calculated according to the 3s criterion (3 times the standard deviation of the measured blanks) and the LOD is given by the 1s criterion. The detec-

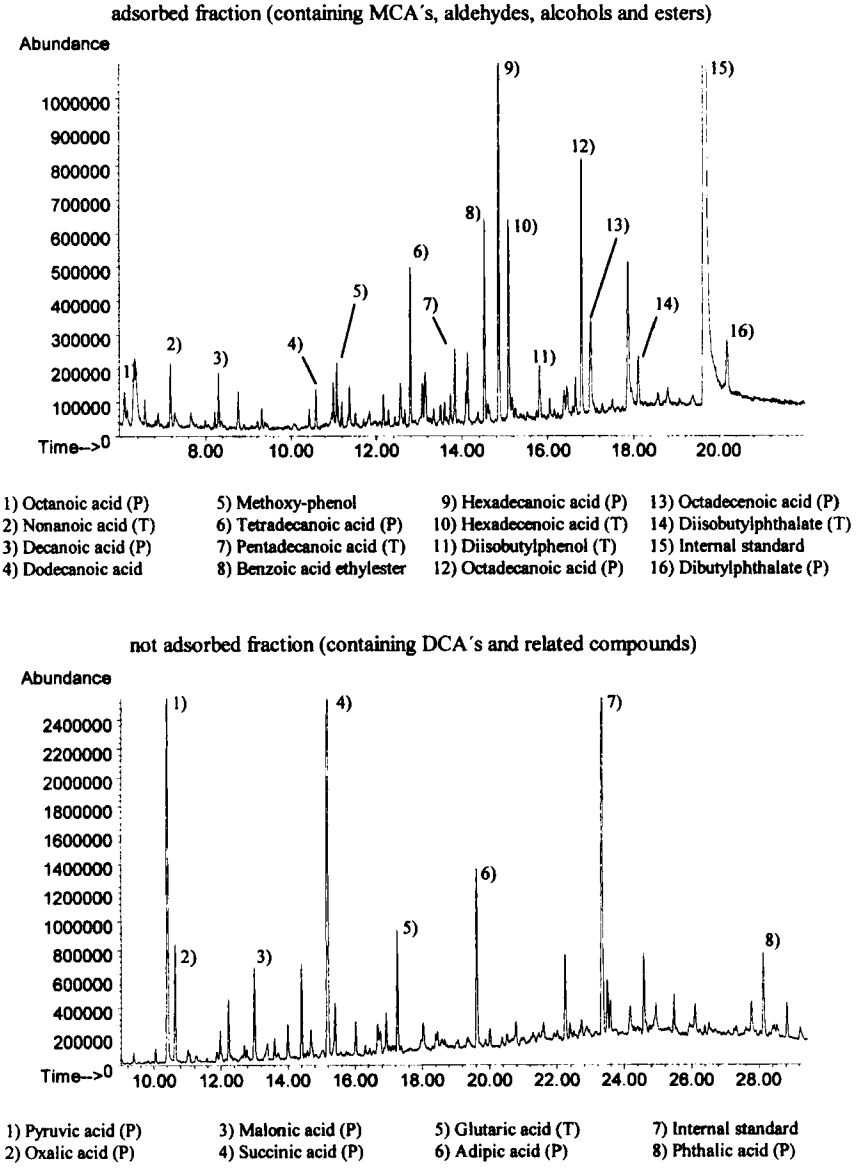

FIGURE 2 Chromatograms from a determined cloud water sample from 30. April 1997

tion and quantification limits for the cloud water and the aerosol samples were calculated from these absolute amounts and the used sample volumes. Table I shows the results for the absolute amounts which are necessary for quantification

and the calculated LOQ values for an average sample volume of 50 m^3 aerosol sample or 50 ml liquid sample. The achieved limits could be improved by obtaining the MS-chromatogram in the single or multiple ion monitoring mode (SIM or MIM).

Aerosol and cloud water samples

For this study 4 aerosol samples and 4 cloud water samples and the corresponding field blanks were used. Figure 2 shows the chromatograms obtained for the adsorbed fraction (containing MCA's, aldehydes, alcohols and esters) and the not adsorbed fraction (containing DCA's and related compounds) from one cloud water sample from the SBO. The mean values (n=4) for all identified and evaluated compounds from the investigated samples are listed in Table II. For compounds obtained with amounts below the LOQ no concentration could be given. In Table II they are marked as detected only. Substances which are marked as tentatively identified could be identified by interpretation and evaluation of characteristic peaks from the mass spectra. For example the MCA's with an odd carbon number could be tentatively identified because their mass spectra show the typical peaks of methyl esters (m/z 74 and m/z 87) and the GC-retention times shows good agreement with the expected values. Library searches for the tentatively identified compounds has shown similar mass spectra to those of the determined compounds (quality factor over 80%).

TABLE II Mean values (n=4) for all identified compounds from the SBO samples

Compound class	*Cloud water*	*Aerosol*
Monocarboxylic Acids	**[ng/ml]**	**[ng/m^3]**
Octanoic acid (P)	1.1	1.2
Nonanoic acid (T)	1.9	5.4
Decanoic acid (P)	0.7	4.7
Undecanoic acid (T)	BDL	1.3
Dodecanoic acid (P)	BDL	3.8
Tetradecanoic acid (P)	BDL	7.7
Pentadecanoic acid (T)	BDL	1.3
Hexadecanoic acid (P)	13.2	13.5
Hexadecenoic acid (T)	3.0	D
Octadecanoic acid (P)	20.8	16.3

Compound class	*Cloud water*	*Aerosol*
Octadecenoic acid (P)	3.2	D
DCA's and related Compounds	**[ng/ml]**	**[ng/m^3]**
Pyruvic acid (P)	50.2	D
Oxalic acid (P)	174.2	9.9
Glyoxal (P)	5.3	2.7
Malonic acid (P)	39.2	0.8
Benzoic acid (P)	2.6	BDL
Succinic acid (P)	85.3	2.9
Glutaric acid (T)	12.9	BDL
Adipic acid (P)	18.3	2.9
Suberic acid (T)	1.7	BDL
Azelaic acid (T)	2.2	D
Phthalic acid (P)	6. 1	1.7
Aromatic Compounds	**[ng/ml]**	**[ng/m^3]**
Ethoxy-alkyl-phenol (T)	3.0	BDL
1 ,4-Dimethoxy-phenol (T)	BDL	7.8
Phenol–4–methoxy-diisobutyl (T)	BDL	15.0
Benzoic acid–4–ethoxy-ethylester (T)	9.6	4.2
Diisobutyl-phenol (T)	3.0	1.8
Diisobutyl-phthalate (T)	0.7	108.1
Dibutyl-phthalate (P)	1.5	13.2
Alcohols	**[ng/ml]**	**[ng/m^3]**
Dodecanol (P)	1.9	3.8
Tetradecanol (P)	D	5.1
Hexadecanol (P)	4.4	7.0
Aldehydes	**[ng/ml]**	**[ng/m^3]**
Nonanal (P)	D	1.8
Benzaldehyde (P)	1.2	0.9
Decanal (P)	0.9	D
Branched aldehyde (C 14) (T)	1.7	BDL
Branched aldehyde (C 15) (T)	1.2	BDL
Branched aldehyde (C 16) (T)	2.2	BDL

(P) ... positively identified. (T) ... tentatively identified. D... compound detected, concentration below LOQ. BDL... below detection limit.

In the aerosol as well as in the cloud water samples some phthalates, phenols, alcohols, aldehydes, MCA's and DCA's could be identified and quantified. The most abundant compounds in the aerosol phase were diisobutylphthalate (108 ng/m^3) followed by octadecanoic acid (16 ng/m^3), phenol-4-methoxy-diisobutyl (15 ng/m^3) hexadecanoic acid (13 ng/m^3) and dibutylphthalate (13 ng/m^3). In the cloud water samples the highest average concentrations were obtained for the dicarboxylic acids. Oxalic acid was found with an average concentration of 174 ng/mL, succinic acid with 85 ng/mL, pyruvic acid with 50 ng/mL and malonic acid with 39 ng/mL. Octadecanoic acid was the MCA with the highest determined average concentration (21 ng/mL). The most abundant aromatic compound was benzoic acid-ethoxy-ethyl-ester (9.6 ng/mL). The phthalates (dominating compounds in the aerosol phase) were obtained with concentrations in the range of only some ng/mL.

For some compound classes an information about the sources could be obtained. The presence of dicarboxylic acids in aerosols and cloud water may result from primary emission and/or secondary photochemical reactions. Although the primary origin of these acids cannot be ruled out, there are no direct biogenic or anthropogenic sources known. For example, particulate abrasion products from leaf surfaces of urban plants were analyzed, and in this samples no dicarboxylic acids were found [12]. Grosjean has suggested that the dicarboxylic acids in the air mass originate from photochemical oxidation of organic compounds like cyclic olefins emitted from anthropogenic sources to the atmosphere [13]. Although direct precursors have not been clearly identified, photochemical oxidation of aromatic hydrocarbons such as benzene and toluene, as well as malonic and succinic acid, have been considered to result in oxalic acid [14]. Dicarboxylic acids are also formed during the autooxidation process of unsaturated lipids by meat cooking operations [15]. Sources contributing saturated n-monocarboxylic acids are similar to the emission sources of n-alkanes. Anthropogenic sources include the combustion of fossil fuels, wood and other biomass [16]. Potential biogenic emission sources are plant waxes, fungi, bacteria, pollen and algae [8]. MCA's <C20 may be derived in part from microbial sources, although these acids are ubiquitous in biota [2]. Furthermore, meat cooking operations and charbroilers have been identified as an important source for monocarboxylic and unsaturated monocarboxylic acids [15]. Phthalates and phenols are emitted from anthropogenic sources. They are industrially used for the production of plastic-materials, cars, furniture and some other applications [17]. Some authors report that they might also originate from biogenic sources, namely from degradation of humic substances [18].

CONCLUSIONS

The developed solid phase extraction method allows the simultaneous determination of different classes of polar organic compounds in atmospheric samples like aerosol or precipitation (rain or snow) samples. Almost all classes of oxygenated organic compounds like mono- and dicarboxylic acids, aldehydes, alcohols or polar aromatic compounds like phthalates with only one sample preparation scheme can be determined.

For the statistical characterization of the method (determination of recoveries and reproducibilities) several standard solutions with a concentration level of 10 μg/L for each compound were analyzed. Generally, the recoveries ranged from 60 – 100%, but only some compounds yielded levels below 80% (e.g. alcohols or acids with 16 or more carbon atoms). The recovery is influenced by the functional groups and the length of the carbon chain of the individual compound, for example the obtained recovery for octadecanol is 61% and for octanol 98%. The reproducibility given as the relative standard deviation varies from 5 to 15%. LOD and LOQ were determined according to 1 time and 3 times standard deviation of the blanks obtained with organic free water. The absolute amount of an individual compound necessary for detection is about 10 to 50 ng. For a volume of 50 ml of a liquid sample or 50 m^3 air LOQ's in a range of 0.5 to 3 ng/mL or ng/m^3, respectively, could be achieved.

The new method was applied for the analysis of 4 aerosol and 4 cloud water samples from a continental background site in Central Europe (Sonnblick Observatory). In all samples a large variety of mono- and dicarboxylic acids were identified and quantified, together with some aldehydes, alcohols and aromatic compounds.

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