A Complete Methodology for the Reliable Collection, Sample Preparation, Separation and Determination of Organic Compounds in Ultrafine 30 nm, 40 nm and 50 nm Atmospheric Aerosol Particles

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ESI-1 Optimization of the individual separation and determination methods, including fragmentation pathways obtained in GC-MS

Table S1. Optimized parameters of the chromatographic conditions (A) and the mass spectrometer (B) for the target analytes analyzed by LC-MS.

(A)

Liquid chromatography Variable	Aldehydes		Diethylamine	
	Tested range	Optimum value	Tested range	Optimum value
Flow-rate (mL min^{-1})	0.1–0.5	0.2	0.2–0.8	0.5
Injection volume (µL)	10.0–100.0	80.0	10.0–100.0	100.0
Initial conditions (% Mobile phase A)	50.0–100.0	90.0	25.0–100.0	50.0
Isocratic time 1 (min)	0.0–5.0	2.0	15.0	
Gradient 1 time (min)	2.0–7.0	4.0	—	
Final composition gradient 1 (% Mobile phase A)	0.0–25.0	10.0	—	
Gradient 2 time (min)	1.0–4.0	2.0	—	
Final composition gradient 2 (% Mobile phase A)	10.0–0.0	0.0	—	
Isocratic time 2	5.0–10.0	7.0	—	
Mobile phase A	Water + 0.1–5% acetic acid	Water + 2% acetic acid	Water + 1.0–5.0% NH_4OH	Water + 2.0 % NH_4OH
Mobile phase B	Acetonitrile + 0.1–5% acetic acid	Acetonitrile +2% acetic acid	Methanol Ethanol Acetonitrile	Acetonitrile

(B)

Mass spectrometry Variable	Method for aldehydes	Method for amines
Capillary (V)	–3900.0	–3350.0
Skimmer (V)	40.0	15.0
Capillary exit (V)	103.5	50.0
Octapole 1(V)	12.0	5.1
Octapole 2 (V)	1.7	0.0
Trap Drive	25.4	20.0
Octapole RF (Vpp)	75.0	50.0
Lens 1(V)	–5.0	–8.9
Lens 2 (V)	–60.0	–73.0

Table S2. Ions (base ions in bold) selected for the determination and/or identification of the target analytes.

A) Polyols*

Analyte	Ions
Levoglucosan	**204**, 217, 333
α. D-mannose	**204**, 191, 217
β. D-mannose	**204**, 191, 217

*GC-MS in SIM mode, splitless injection at 280°C, helium as carrier gas 1.3 mL/min, oven programmed from 65°C (2 min) to 300°C (15 min) at 6°C/min, electron ionization (70 eV). 1,1´-binaphthyl was used as internal standard.

B) Acids*

Analyte	Ions
Malonic acid	**147**, 117,219,190
Maleic acid	**147**, 245, 116, 260
Malic acid	**147**, 233, 245
Adipic acid	**111**, 275, 147
Azelaic acid	**317**, 201, 147, 129
Tartaric acid	**292**, 219, 147
Stearic acid	**117**, 129, 145, 341
Oleic acid	**117**, 129, 145, 339
Palmitic acid	**117**, 313, 129, 145
Vanillic acid	**297**, 312, 267
cis-Pinonic acid	**171**, 124, 83
3-Hydroxyglutaric acid	**147**, 349,185,259
Pinic acid	**129**, 171, 157
Benzoic acid	**179,**135,105
Mandelic acid	**179,** 117, 129
Sebacic acid	**331,** 215, 129

*GC-MS in SIM mode, splitless injection at 280°C, helium as carrier gas 1.0 mL/min, oven programmed from 60°C (4 min) to 140°C (6 min) at 6°C/min, then to 190°C (4 min) at 5 °C/min, then to 210 at 5 °C/min, and finally to 270°C (5 min) at 20 °C/min, electron ionization (70 eV). 1,1´-binaphthyl was used as internal standard.

C) Aldehydes*

Analyte	MM	Ions
Pinonaldehyde	166	167
β-Caryophyllene aldehyde	236	237
β-Nocaryophyllene aldehyde	238	239
Benzaldehyde	106	107
Hexanal	100	101
Octanal	128	129
Nonanal	142	143
Tridecanal	198	199

*LC-MS, selected precursor ion for all the analytes was $[M+H]^+$. Octanal-d_3 was used as internal standard.

D) Amines*

Analyte	MM	Ions
Diethylamine	73	74
Ethylenediamine	60	61
Dipropylamine	101	102
p-Aminophenol	109	110
Isopropylamine	59	60
Isopropylanyline	135	136
Tripropylamine	143	144

*LC-MS, 2-pyridylbenzoimidazole was used as internal standard.

ESI-2 Optimization of the methods developed for the determination of target analytes in aerosol particles

Table S3

A) Tested and optimum values for the variables of the extraction procedure.* A multivariate design —Plackett-Burman design 2^6 x 3/16 type III resolution allowing 8 degrees of freedom and involving 12 randomized runs plus three centre points— was used for the optimization of the variables

Variable	Tested	Optimum
Probe position (cm)	0–2	2
Amplitude (%)**	10–50	50
Duty Cycle (%)	10–50	50
Flow-rate (ml/min)	0.25–1	1
Extraction time (min)	5-25	20
Extractant composition (acetone:metanol)	1:1–0:1	0:1

*After the extraction 3 drops of toluene was added as a keeper, extraction solvent was evaporated using rotary evaporator, and extract diluted to 5 mL with methanol. Decafluorobenzophenone was used as an internal standard for the extraction.
**Of the applied power (100 W) of the converter

B) Tested and optimum values for the variables of the derivatization procedure. 2,4-dichlorobenzoic acid was used as an internal standard for derivatization. A multivariate design —half fraction design 2^{4-1} type IV resolution allowing 3 degrees of freedom and involving 8 randomized runs plus three centre points— was used for the optimization of the variables

Variable	Tested	Optimum
Sample volume (µl)	500-2000	2000
Pyridine: BSTFA 1% TMCS volume (µl)	20-50	40
Pyridine:BSTFA composition	2:1-1:2	1:1
Temperature (ºC)	20:40	35
Duty cycle (%)	10-50	10
Amplitude (%)*	10-70	70
Probe position (cm)**	1-3	1.5
Derivatization time (min)***	5-50	30

*of the applied power (140W) of the converter
**Distance from the reaction vial
***Time the reaction mixture was under ultrasounds. Mixture was shaken vigorously in the vial for additional 5 min before applying ultrasounds.

ESI-3. Validation of the methods developed

Table S4. Method characteristics

A) Acids

Analyte	Calibration curve	Linear range[a]	r^2	LOD[b]	LOQ[b]
3-Hydroxyglutaric acid	$Y= 6.0\ 10^{-5}X +4.2\ 10^{-3}$	2000–LOQ	0.994	20	60
Adipic acid	$Y= 2.0\ 10^{-4}X +4.5\ 10^{-3}$	2000–LOQ	0.995	40	140
Azelaic acid	$Y= 9.0\ 10^{-5}X –1.0\ 10^{-2}$	2000–LOQ	0.992	20	80
Palmitic acid	$Y= 3.0\ 10^{-4}X +1.3\ 10^{-2}$	2000–LOQ	0.991	20	80
Maleic acid	$Y= 3.0\ 10^{-4}X +2.3\ 10^{-3}$	2000–LOQ	0.998	20	80
Malic acid	$Y= 2.0\ 10^{-4}X –8.4\ 10^{-3}$	2000–LOQ	0.997	60	200
Malonic acid	$Y= 6.0\ 10^{-4}X –2.0\ 10^{-2}$	2000–LOQ	0.996	20	80
Stearic acid	$Y= 2.0\ 10^{-4}X +1.0\ 10^{-2}$	2000–LOQ	0.998	40	160
Oleic acid	$Y= 1.0\ 10^{-4}X –1.0\ 10^{-2}$	2000–LOQ	0.992	20	100
Pinic acid	$Y= 1.0\ 10^{-4}X +3.4\ 10^{-2}$	2000–LOQ	0.995	40	120
Pinonic acid	$Y= 1.0\ 10^{-4}X +2.7\ 10^{-2}$	2000–LOQ	0.997	60	200
Tartaric acid	$Y= 3.0\ 10^{-4}X +1.0\ 10^{-2}$	2000–LOQ	0.998	40	160
Vanillic acid	$Y= 2.0\ 10^{-4}X –3.2\ 10^{-2}$	2000–LOQ	0.998	40	160
Benzoic acid	$Y= 5.0\ 10^{-5}X –7.0\ 10^{-3}$	2000-LOQ	0.998	40	160
Mandelic acid	$Y= 2.0\ 10^{-3}X –1.3\ 10^{-2}$	2000-LOQ	0.999	20	80
Sebacic acid	$Y= 2.0\ 10^{-4}X –1.5\ 10^{-3}$	2000-LOQ	0.997	20	80

[a] Expressed as ng, [b] expressed as pg

B) Polyols

Analyte	Calibration curve	Linear range[a]	r^2	LOD[b]	LOQ[b]
Levoglucosan	$Y= 2.6\ 10^{-3}X +9.2\ 10^{-3}$	2000–LOQ	0.997	200	800
α.- *D*-mannose	$Y= 6.8\ 10^{-3}X +3.9\ 10^{-2}$	760–LOQ	0.997	200	400
β- *D*-mannose	$Y= 6.8\ 10^{-3}X +4.8\ 10^{-2}$	1240–LOQ	0.998	60	200

[a] Expressed as ng, [b] expressed as pg

C) Aldehydes

Analyte	Calibration curve	Linear range[a]	r^2	LOD[b]	LOQ[b]
Pinonaldehyde	$Y= 5.9\ 10^{-4}X +5.0\ 10^{-3}$	500–LOQ	0.996	20	66
Benzaldehyde	$Y= 1.0\ 10^{-3}X +1.0\ 10^{-4}$	500–LOQ	0.999	12	42
β-Caryophyllene aldehyde	$Y= 8.8\ 10^{-4}X +6.0\ 10^{-4}$	500–LOQ	0.992	60	200
β-Nocaryophyllene aldehyde	$Y= 9.4\ 10^{-4}X +5.6\ 10^{-4}$	500–LOQ	0.993	80	240
Hexanal	$Y= 1.4\ 10^{-2}X +3.3\ 10^{-4}$	500–LOQ	0.997	60	200

Octanal	$Y= 2.0\ 10^{-3}X +2.8\ 10^{-4}$	500–LOQ	0.998	20	66
Nonanal	$Y= 2.0\ 10^{-3}X +2.4\ 10^{-4}$	500–LOQ	0.999	20	66
Tridecanal	$Y= 1.7\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.996	60	200

[a] Expressed as ng, [b] expressed as pg

D) Amines

Analyte	Calibration curve	Linear range[a]	r^2	LOD[b]	LOQ[b]
Diethylamine	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.998	6	20
Ethylenediamine	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.997	12	39
Dipropylamine	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.999	32	101
p-Aminophenol	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.998	41	133
Isopropylamine	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.996	44	140
Isopropylaniline	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.997	60	200
Tripropylamine	$Y= 3.8\ 10^{-3}X +2.1\ 10^{-4}$	500–LOQ	0.999	22	75

[a] Expressed as ng, [b] expressed as pg

Table S5. Repeatability (s_b) and within-laboratory reproducibility (s_{wd}) expressed as relative standard deviation (RSD) for aerosol samples

A) Acids

Sample ID	Forest (50 nm)		Forest (TS)		Urban (50 nm)		Urban (TS)	
	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}
Maleic acid	4.4	8.2	0.3	0.4	5.3	6.1	2.0	2.6
Malonic acid	4.7	6.3	0.4	0.7	—	—	1.0	1.2
Malic acid	3.1	3.2	1.7	2.6	1.1	1.6	1.1	1.8
Adipic acid	—	—	—	—	0.4	0.6	0.5	0.8
Azelaic acid	3.2	4.2	0.4	0.5	1.7	3.5	0.7	1.5
Tartaric acid	—	—	—	—	—	—	2.3	3.6
Stearic acid	1.9	6.8	0.3	0.7	0.6	0.9	0.2	2.0
Oleic acid	5.3	5.9	0.8	0.9	0.8	3.1	1.1	1.2
Palmitic acid	2.9	4.8	0.2	0.6	0.7	1.3	0.5	1.1
Vanillic acid	—	—	—	—	—	—	2.7	3.0
Pinic acid	—	—	—	—	—	—	0.4	0.6
Hydroxyglutaric acid	6.0	7.2	0.8	1.3	0.3	0.4	1.0	1.9
Pinonic acid	2.9	3.6	0.9	1.2	1.3	2.4	1.8	2.0
Mandelic acid	—	—	—	—	—	—	—	—
Benzoic acid	4.4	5.3	1.8	2.1	3.3	4.2	2.1	3.2
Sebacic acid	—	—	—	—	—	—	—	—

B) Polyols

Sample ID	Forest (50 nm)		Forest (TS)		Urban (50 nm)		Urban (TS)	
	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}
Levoglucosan	2.7	5.9	1.5	6.3	3.2	3.7	3.5	3.8
α-D-mannose	2.5	3.4	—	—	3.2	3.4	0.9	1.8
β- D-mannose	—	—	—	—	5.5	9.4	2.0	2.3

C) Aldehydes

Sample ID	Forest (50 nm)		Forest (TS)		Urban (50 nm)		Urban (TS)	
	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}
Pinonaldehyde	6.5	6.8	7.5	7.6	4.4	4.8	7.5	8.1
β-caryophyllene aldehyde	5.1	5.4	6.3	6.7	6.6	5.8	9.4	9.7
β-nocaryophyllene aldehyde	3.8	4.1	3.3	3.7	6.8	7.1	8.5	9.0
Benzaldehyde	1.2	1.4	2.1	2.3	2.2	2.5	8.1	8.2
Hexanal	2.4	2.9	4.4	6.1	3.3	4.7	3.1	4.1
Octanal	3.3	4.3	3.9	5.5	4.2	5.6	2.9	3.7
Nonanal	4.1	5.4	2.1	4.1	1.9	2.5	4.2	5.5
Tridecanal	—	—	1.9	2.8	—	—	—	—

D) Amines

Sample ID	Forest (50 nm)		Forest (TS)		Urban (50 nm)		Urban (TS)	
	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}	s_b	s_{wr}
Ethylenediamine	3.7	5.5	4.5	6.1	5.2	7.3	6.5	8.3
Diethylamine	__	__	__	__	4.1	5.0	1.2	1.3
Dipropylamine	5.5	6.3	__	__	4.4	6.4	4.3	5.8
p-Aminophenol	__	__	__	__	3.9	5.4	6.2	7.1
Isopropylamine	__	__	__	__	4.1	8.1	4.3	6.6
Isopropylaniline	__	__	__	__	2.9	3.3	3.3	4.5
Tripropylamine	2.9	4.4	__	__	__	__	__	__

Table S6. Accuracy of the method and potential matrix effect study (errors, in parenthesis, expressed as percentage, n=5, replicates). Recovery expressed as %

A) Acids

Sample ID	Forest (50 nm)			Forest (TS)			Urban (50 nm)			Urban (TS)		
	Found[a]	Recovery		Found[a]	Recovery		Found[a]	Recovery		Found[a]	Recovery	
		L1	L2		L1	L2		L1	L2		L1	L2
Malonic acid	0.3 (2.2)	99.8	100.0	0.2(0.5)	99.9	99.6	<LOQ	99.9	99.9	2.5(0.5)	100.0	99.8
Maleic acid	1.6(2.4)	98.7	100.0	0.6(0.8)	100.0	100.0	11.6(3.3)	100.0	99.9	2.3(2.8)	99.3	100.1
Malic acid	0.3(1.6)	100.1	100.7	0.1(0.9)	100.2	100.3	0.3(0.6)	99.4	99.8	2.0(0.6)	99.9	99.6
Adipic acid	<LOQ	101.3	99.9	<LOQ	100.0	99.9	2.7(0.3)	99.9	99.9	0.9(0.3)	99.9	99.2

Azelaic acid	2.6(1.6)	100.2	99.2	0.8(0.2)	100.0	99.9	1.5(0.8)	99.6	99.9	1.4(0.4)	99.1	100.6
Tartaric acid	<LOQ	95.9	99.6	ND	99.8	99.1	<LOQ	100.0	99.9	0.7(1.3)	100.3	100.4
Stearic acid	20.2(1.0)	99.5	101.5	6.4(0.4)	100.3	100.3	17.6(0.3)	98.9	100.5	21.7(0.1)	100.2	100.0
Oleic acid	24.8(2.7)	104.6	99.6	8.2(0.6)	99.9	99.9	24.1(0.4)	99.3	100.5	15.1(0.5)	100.0	100.7
Palmitic acid	32.0(1.4)	102.2	97.7	12.2(1.0)	100.0	100.0	35.1(0.5)	100.2	100.3	47.2(0.3)	99.3	100.0
Vanillic acid	ND	102.5	100.2	ND	100.0	100.0	<LOQ	100.0	99.9	0.3(1.4)	100.2	99.8
Pinonic acid	2.0(0.4)	102.5	100.1	0.6(0.4)	100.1	100.2	1.8(0.6)	100.0	99.9	0.5(0.9)	100.0	100.2
3-HGA	0.9(3.0)	100.8	100.5	0.6(0.4)	94.7	99.9	2.6(0.4)	100.0	99.9	1.5(0.5)	100.0	100.0
Pinic acid	<LOQ	100.4	100.0	<LOQ	99.9	99.8	<LOQ	99.8	99.9	0.3(0.5)	100.5	100.5
Benzoic acid	3.8(4.1)	100.1	99.8	2.2(1.1)	102.1	100.1	1.4(1.5)	97.9	102.1	0.2(1.3)	99.6	101.2
Mandelic acid	ND	99.8	100.2	ND	99.8	101.2	ND	100.3	101.5	ND	103.1	101.1
Sebacic acid	ND	98.7	101.1	ND	96.9	98.9	ND	98.6	102.4	ND	100.1	99.8

3-HGA, 3-Hydroxyglutaric acid.

B) Polyols

Sample ID	Forest (50 nm)			Forest (TS)			Urban (50 nm)			Urban (TS)		
	Found[a]	Recovery		Found[a]	Recovery		Found[a]	Recovery		Found[a]	Recovery	
		L1	L2		L1	L2		L1	L2		L1	L2
Levoglucosan	0.2(1.6)	99.9	102.2	0.3(0.8)	96.7	98.6	19.1(1.8)	96.2	99.9	27.4(2.1)	100.0	99.8
α- *D*-mannose	0.2(1.8)	96.7	97.7	<LOQ	104.3	96.9	9.1(1.6)	98.2	97.0	17.7(0.6)	99.3	100.1
β- *D*-mannose	<LOQ	100.9	96.5	<LOQ	103.8	98.4	38.9(2.3)	98.0	99.2	48.1(1.1)	99.9	99.6

C) Aldehydes

Sample ID	Forest (50 nm)			Forest (TS)			Urban (50 nm)			Urban (TS)		
	Found[a]	Recovery		Found[a]	Recovery		Found[a]	Recovery		Found	Recovery	
		L1	L2		L1	L2		L1	L2		L1	L2
Pinonaldehyde	0.2(3.4)	101.3	99.8	0.3(3.6)	100.9	98.7	10.3(2.4)	100.0	101.1	1.8(3.7)	100.6	100.1
β-Caryophyllene aldehyde	0.1(2.5)	100.4	100.7	0.1(3.3)	99.3	101.2	11.9(3.4)	99.9	99.5	0.8(4.6)	99.7	98.9
β-Nocaryophyllene aldehyde	0.1(1.7)	99.8	98.5	0.1(1.6)	97.5	102.4	9.7(3.4)	98.6	101.3	0.6(4.4)	102.0	100.1
Benzaldehyde	0.7(0.8)	98.7	102.2	1.4(1.1)	102.1	100.1	3.5(1.4)	98.8	100.2	0.7(4.2)	101.4	99.6
Hexanal	4.2(1.3)	97.6	101.1	2.8(2.1)	100.4	97.1	10.4(2.2)	99.6	98.2	2.1(1.7)	99.6	101.4
Octanal	0.8(1.7)	98.4	99.9	2.6(1.9)	100.7	99.8	4.8(2.3)	101.2	101.7	0.4(2.1)	98.7	100.1
Nonanal	0.7(2.2)	99.2	99.8	0.4(1.3)	101.3	100.1	6.6(0.8)	97.8	100.1	0.2(2.3)	99.9	102.1
Tridecanal	<LOQ	100.1	100.4	5.2	100.8	101.2	ND	101.5	102.2	ND	101.1	100.8

D) Amines

Sample ID	Forest (50 nm)		Forest (TS)		Urban (50 nm)		Urban (TS)	
	Found[a]	Recovery	Found[a]	Recovery	Found[a]	Recovery	Found[a]	Recovery

		L1	L2		L1	L2		L1	L2		L1	L2
Ethylenediamne	0.2(1.9)	99.2	101.3	0.1(4.1)	102.1	100.8	4.5(2.8)	99.7	102.1	2.0(3.6)	100.4	99.6
Diethylamine	<LOQ	103.2	96.5	<LOQ	97.6	99.4	2.2(2.1)	98.6	101.2	0.3(0.6)	99.3	100.2
Dipropylamine	0.5(2.5)	98.9	100.6	<LOQ	100.3	99.7	4.3(2.2)	101.2	99.4	0.3(2.6)	99.8	98.7
p-Aminophenol	<LOQ	97.9	101.2	<LOQ	99.4	100.3	5.9(2.1)	100.3	101.2	5.6(3.6)	97.9	100.1
Isopropylamine	<LOQ	98.7	100.9	<LOQ	97.8	100.1	0.1(2.2)	102.1	100.1	0.1(2.7)	101.3	98.7
Isopropylaniline	<LOQ	99.6	100.6	<LOQ	100.5	101.2	2.8(1.6)	100.8	98.7	0.6(1.6)	102.1	100.2
Tripropylamine	0.4(1.6)	101.1	99.8	<LOQ	101.1	100.5	<LOQ	101.7	99.8	<LOQ	98.6	99.9

[a]Expressed as ng m^{-3}

Table S7. Comparison of the extraction method developed to Soxhlet extraction for selected marker compounds. Number of analyzed samples in brackets. All results are expressed as ng m^{-3}.

A) Acids

	Soxhlet (12)					Ultrasounds (12)				
	Mean	Min	Max	Variance	Median	Mean	Min	Max	Variance	Median
Malonic acid	0.150	ND	0.800	0.055	0.25	0.150	ND	0.800	0.055	0.050
Maleic acid	0.275	0.100	0.700	0.035	0.25	0.275	0.10	0.700	0.035	0.250
Malic acid	0.067	ND	0.300	0.010	0.10	0.067	ND	0.300	0.010	0.000
Adipic acid	0.025	ND	0.100	0.002	0.10	0.025	ND	0.100	0.002	0.000
Azelaic acid	0.425	ND	2.300	0.598	1.25	0.417	ND	2.300	0.602	0.000
Tartaric acid	—	—	—	—	—	—	—	—	—	—
Stearic acid	3.567	0.200	6.700	5.339	3.000	3.575	0.20	6.700	5.466	3.000
Oleic acid	8.567	ND	26.500	56.793	8.050	8.542	ND	26.400	56.401	8.050
Palmitic acid	22.567	11.100	37.600	50.086	22.650	22.575	11.00	37.800	51.195	22.650
Vanillic acid	0.008	ND	0.100	0.001	0.000	0.008	ND	0.100	0.001	0.000
cis-Pinonic acid	0.042	ND	0.100	0.003	0.000	0.042	ND	0.100	0.003	0.000
3-HGA*	0.108	ND	0.300	0.008	0.100	0.108	ND	0.300	0.008	0.100
Pinic acid	0.042	ND	0.100	0.003	0.000	0.042	ND	0.100	0.003	0.000
Mandelic acid	0.033	ND	0.100	0.002	0.000	0.033	ND	0.100	0.002	0.000
Benzoic acid	—	—	—	—	—	—	—	—	—	—
Sebacic acid	—	—	—	—	—	—	—	—	—	—

*3-HGA. 3-Hydroxyglutaric acid.
ND, Not detectable

B) Polyols

	Soxhlet (12)					Ultrasounds (12)				
	Mean	Min	Max	Variance	Median	Mean	Min	Max	Variance	Median
Levoglucosan	3.79	0.20	16.20	18.09	3.45	3.89	0.20	16.50	18.87	3.45
α- *D*-mannose	0.28	0.10	1.40	0.15	0.10	0.28	0.10	1.40	0.15	0.10
β- *D*-mannose	1.07	0.10	5.90	2.78	0.45	1.07	0.10	6.00	2.84	0.45

ND, Not detectable

C) Aldehydes

	Soxhlet (12)					Ultrasounds (12)				
	Mean	Min	Max	Variance	Median	Mean	Min	Max	Variance	Median
Pinonaldehyde	1.425	0.40	2.900	0.491	1.250	1.433	0.400	2.900	0.504	1.250
β-Caryophyllene aldehyde	0.625	0.20	1.800	0.278	0.300	0.625	0.200	1.800	0.278	0.300
β-Nocaryophyllene aldehyde	1.200	0.50	2.200	0.404	1.000	1.208	0.500	2.300	0.423	1.000
Benzaldehyde	0.057	ND	0.110	0.003	0.090	0.058	ND	0.110	0.003	0.090
Hexanal	0.045	ND	0.130	0.003	0.000	0.044	ND	0.120	0.003	0.000
Octanal	0.052	ND	0.120	0.003	0.050	0.057	ND	0.120	0.004	0.050
Nonanal	0.038	ND	0.120	0.003	0.000	0.034	ND	0.110	0.003	0.000
Tridecanal	0.043	ND	0.120	0.003	0.000	0.045	ND	0.120	0.003	0.000

ND, Not detectable

D) Amines

	Soxhlet (12)					Ultrasounds (12)				
	Mean	Min	Max	Variance	Median	Mean	Min	Max	Variance	Median
Ethylenediamine	0.047	ND	0.150	0.003	0.000	0.043	ND	0.130	0.003	0.000
Diethylamine	0.073	ND	0.140	0.003	0.090	0.067	ND	0.120	0.002	0.100
Dipropylamine	0.033	ND	0.100	0.002	0.000	0.038	ND	0.150	0.003	0.000
p-Aminophenol	0.065	ND	0.130	0.003	0.080	0.073	ND	0.130	0.003	0.100
Isopropylamine	0.040	ND	0.100	0.002	0.000	0.046	ND	0.140	0.003	0.000
Isopropylanyline	0.044	ND	0.130	0.003	0.000	0.042	ND	0.100	0.003	0.000
Tripropylamine	0.019	ND	0.130	0.002	0.000	0.020	ND	0.140	0.002	0.000

ND, Not detectable