

SUPPLEMENTARY INFORMATION

Volatile organic compound fragmentation in the afterglow of pulsed glow discharge in ambient air

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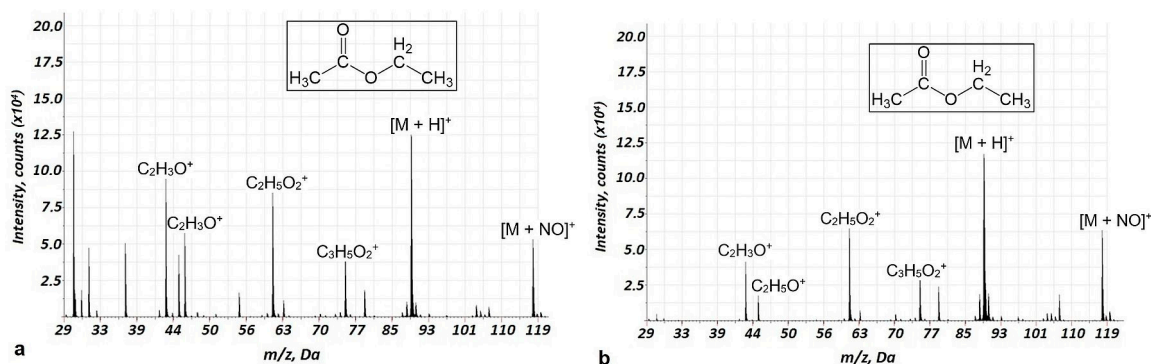


Figure S1. Background corrected mass spectrum range of ethyl acetate (70 ppm) obtained using a flat silicon cathode for the air-argon (a) and air (b) glow discharge. Acquisition parameters: repelling pulse delay 200 μ s, pulse duration 1.0 μ s, pulse period 900 μ s, air pressure 160 Pa, argon pressure 33 Pa.

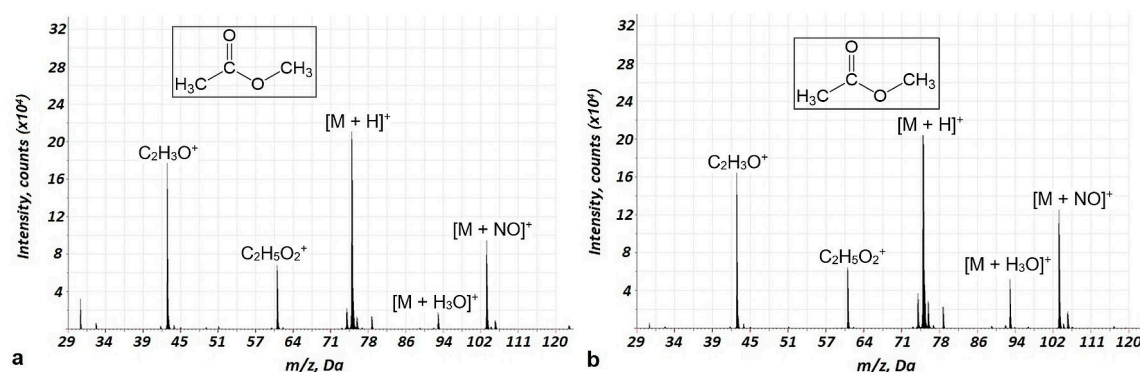


Figure S2. Background corrected mass spectrum range of methyl acetate (70 ppm) obtained using a flat silicon cathode for the air-argon (a) and air (b) glow discharge. Acquisition parameters: repelling pulse delay 200 μ s, pulse duration 1.0 μ s, pulse period 900 μ s, air pressure 160 Pa, argon pressure 33 Pa.

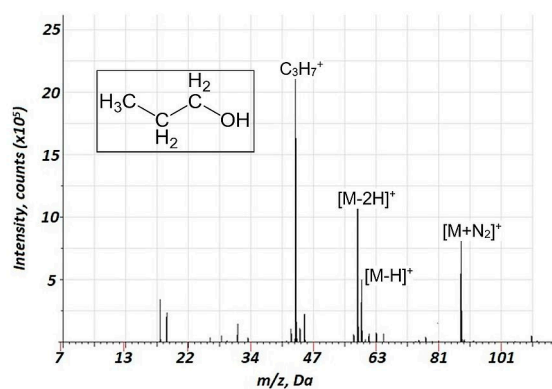


Figure S3 Background corrected mass spectrum range of propanol-1 (50 ppm) obtained using flat copper cathode air glow discharge. Acquisition parameters: repelling pulse delay 100 μ s, pulse duration 1.2 μ s, pulse period 300 μ s, air pressure 133 Pa.

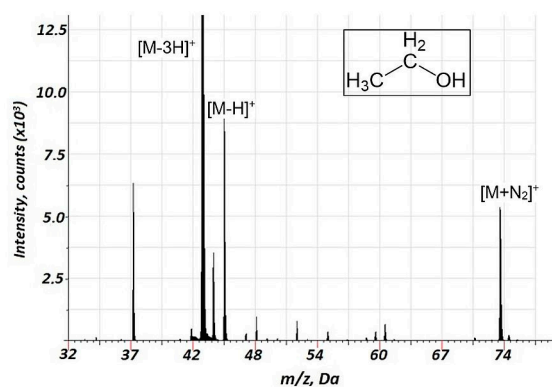


Figure S4. Background corrected mass spectrum range of ethanol (100 ppm) obtained with a flat copper cathode for air glow discharge (Penning ionization). Acquisition parameters: repelling pulse delay 100 μ s, pulse duration 1.2 μ s, pulse period 300 μ s, air pressure 133 Pa.

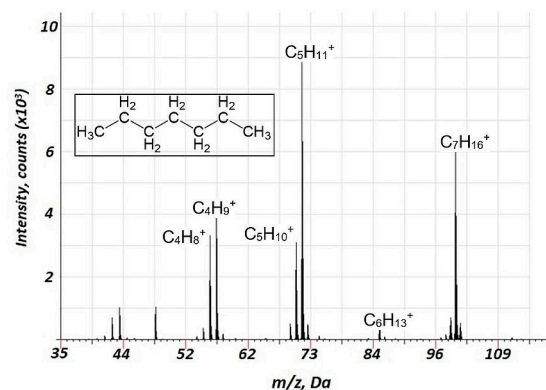


Figure S5. Background corrected mass spectrum of heptane (50 ppm) obtained using a flat copper cathode for air glow discharge. Acquisition parameters: repelling pulse delay 200 μ s, pulse duration 1.2 μ s, pulse period 900 μ s, air pressure 133 Pa.

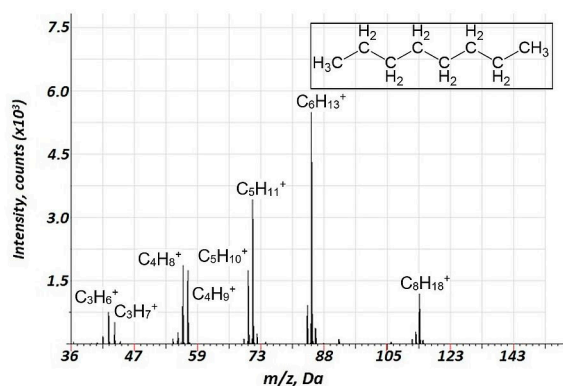


Figure S6. Background corrected mass spectrum range of octane (70 ppm) obtained using a flat silicon cathode for air glow discharge (Penning ionization). Acquisition parameters: repelling pulse delay 200 μ s, pulse duration 1.0 μ s, pulse period 900 μ s, air pressure 160 Pa, argon pressure 33 Pa.

Table S1. Binding energies for some volatile organic compounds according to NIST database [1].

Compound	Ionization energy, eV	Fragment	Energy, eV	Residue
Alkanes				
n-Hexane	10.2	C ₃ H ₆ ⁺	11	C ₃ H ₈
		C ₃ H ₇ ⁺	11.4	C ₃ H ₇
		C ₄ H ₈ ⁺	11	C ₂ H ₆
		C ₄ H ₉ ⁺	11.1	C ₂ H ₅
		C ₅ H ₁₀ ⁺	11	CH ₄
		C ₅ H ₁₁ ⁺	11.1	CH ₃
Cyclohexane	9.9	C ₃ H ₆ ⁺	11.2	C ₃ H ₆
		C ₃ H ₇ ⁺	11.5-13.5	C ₃ H ₅
		C ₄ H ₇ ⁺	11.2	C ₂ H ₅
		C ₄ H ₈ ⁺	11.1-11.5	C ₂ H ₄
		C ₅ H ₉ ⁺	9.9-11.2	CH ₃
		C ₆ H ₁₁ ⁺	11.3-11.7	H
n-Heptane	9.9	C ₃ H ₆ ⁺	10.7 -10.9	C ₄ H ₁₀
		C ₃ H ₇ ⁺	11.1-11.6	No data*
		C ₄ H ₇ ⁺	11.5	No data
		C ₄ H ₈ ⁺	10.6-11.0	C ₃ H ₈
		C ₄ H ₉ ⁺	10.6-11.2	C ₃ H ₇
		C ₅ H ₁₀ ⁺	10.3-11.0	C ₂ H ₆
		C ₅ H ₁₁ ⁺	10.4-11.0	C ₂ H ₅
		C ₆ H ₁₂ ⁺	11.2	CH ₄
		C ₆ H ₁₃ ⁺	10.7 -10.9	CH ₃
n-Octane	9.8	C ₃ H ₇ ⁺	11.9	No data
		C ₄ H ₈ ⁺	11.1-11.4	C ₄ H ₁₀ /n-C ₄ H ₉ No data
		C ₅ H ₁₀ ⁺	11.1	C ₃ H ₈
		C ₅ H ₁₁ ⁺	11.0-11.2	C ₃ H ₇

		$C_6H_{12}^+$	10.3-10.8	C_2H_6
		$C_6H_{13}^+$	10.9	C_2H_5
		$C_7H_{15}^+$	10.9	CH_3
n-Nonane	10.2	$C_4H_9^+$	11.2	No data
		$C_5H_{11}^+$	11.1	C_4H_9
		$C_6H_{13}^+$	10.6	No data
n-Decane	9.7		No data	
n-Undecane	9.6		No data	
n-Dodecane	10.4	$C_6H_{12}^+$	10.4	No data
Alcohols				
Methanol	10.84		> 12	
Ethanol	10.47	CH_3O^+	11.2-11.4	CH_3
		$C_2H_5O^+$	10.6-10.8	H
Propanol-1	10.15	CH_3O^+	11.1-12.3	C_2H_5
		$C_2H_5O^+$	11.1-11.4	CH_3
		$C_3H_6^+$	10.3-10.7	H_2O
		$C_3H_7O^+$	10.2-10.7	H
Propanol-2	10.1	$C_2H_4O^+$	10.2-10.3	CH_4
		$C_2H_5O^+$	10.2-10.7	CH_3
		$C_3H_7O^+$	10.3-11.9	H
Butanol-1	10.04	CH_3O^+	11.4	n- C_3H_7
		$C_2H_2O^+$	11.2	No data
		$C_4H_8O^+$	10.2	H_2O
Isobutanol	10.12	CH_5O^+	10.4-10.5	C_3H_5
		$C_3H_6^+$	11.0 -11.3	CH_3OH
		$C_4H_8^+$	10.3	H_2O
Butanol-2	10.1	$C_2H_4O^+$	10.1	C_2H_6
		$C_2H_5O^+$	10.2-10.4	C_2H_5
		$C_3H_6O^+$	10.2	CH_4
		$C_3H_7O^+$	10.1-10.7	CH_3
		$C_3H_8O^+$	10.2	CH_4
Pentanol-1	10.38	$C_5H_{10}^+$	10	H_2O
Pentanol-2	9.78	$C_2H_5O^+$	10.2	1- C_3H_7
Isoamyl alcohol	No data		No data	
Hexanol-1	10.35	$C_2H_4O^+$	10.7	No data
		$C_4H_8O^+$	9.9	No data

Benzyl alcohol	9.23	C ₆ H ₇ ⁺	10.3-10.9	No data
		C ₇ H ₇ O ⁺	10.0-10.5	No data
Carbonyle compounds				
Formaldehyde	10.9	CHO ⁺	11.9	H
Ethanal	10.2	C ₂ H ₂ O ⁺	10.7 -13.1	H ₂
		C ₂ H ₃ O ⁺	10.5-11.0	H
Propanal	9.9	C ₂ H ₃ O ⁺	10.8	CH ₃
		C ₃ H ₅ O ⁺	10.2	H
Butanal	9.8	C ₂ H ₃ O ⁺	10.2	C ₂ H ₅
		C ₂ H ₄ O ⁺	10.5	C ₂ H ₄
		C ₃ H ₅ O ⁺	10.2	No data
Pentanal	9.7	C ₂ H ₄ O ⁺	11.4	C ₃ H ₆
		C ₃ H ₆ ⁺	11.9	C ₂ H ₄ O
		C ₃ H ₆ O ⁺	9.8-10.0	C ₂ H ₄
		C ₅ H ₈ ⁺	9.8-10.0	H ₂ O
Hexanal	9.8	C ₂ H ₄ O ⁺	11.6	C ₄ H ₈
		C ₃ H ₆ O ⁺	10.2	C ₃ H ₆
		C ₃ H ₆ O ⁺	9.7	C ₃ H ₆
		C ₄ H ₈ ⁺	10.7	C ₂ H ₄ O
		C ₄ H ₈ O ⁺	10	C ₃ H ₆
		C ₆ H ₁₀ O ⁺	9.8	H ₂ O
Heptanal	9.65		No data	
Acetone	9.7	C ₂ H ₂ O ⁺	10.7	CH ₄
		C ₂ H ₃ O ⁺	10.3-12.2	CH ₃
Carboxylic acids				
Formic acid	11.1		> 12	
Acetic acid	10.7	C ₂ H ₃ O ⁺	11.4-11.8	OH
Propanoic acid	10.2	C ₃ H ₄ O ⁺	10.9-11.6	H ₂ O
		C ₃ H ₅ O ⁺	11.0-12.2	OH
		C ₃ H ₅ O ₂ ⁺	11.1-11.7	H
Butanoic acid	10.2	C ₂ H ₄ ⁺	11.5	C ₂ H ₄ O ₂
		C ₂ H ₄ O ₂ ⁺	10.4-10.6	C ₂ H ₄
		C ₂ H ₅ ⁺	11.6	C ₂ H ₃ O ₂
		C ₂ H ₄ O ₂ ⁺	10.6	C ₂ H ₄
		C ₃ H ₅ O ₂ ⁺	10.5	CH ₃

		C ₃ H ₆ ⁺	11.4	CH ₂ O ₂
		C ₃ H ₇ ⁺	11	COOH
		C ₄ H ₇ O ⁺	11.8	OH
Arenes				
Benzene	9.2		> 12	
Toluene	8.8	C ₇ H ₇ ⁺	10.7-11.8	H
		C ₇ H ₇ ⁺ [C ₆ H ₅ CH ₂ ⁺]	10.7 -11.2	H
		C ₇ H ₇ ⁺ [c- C ₇ H ₇ ⁺]	10.5-11.1	H
Ethylbenzene	8.8	C ₆ H ₆ ⁺	11	C ₂ H ₄
		C ₇ H ₇ ⁺	9.9-10.9	CH ₃
		C ₈ H ₉ ⁺	10.6-12.1	H
o-Xylene	8.6	C ₇ H ₇ ⁺	11.1-11.8	CH ₃
		C ₈ H ₉ ⁺	11.3-12.1	H
m-Xylene	8.6	C ₇ H ₇ ⁺	11.3-11.8	CH ₃
		C ₈ H ₉ ⁺	11.7-12.3	H
p-Xylene	8.4	C ₇ H ₇ ⁺	11.1-11.9	CH ₃
		C ₈ H ₉ ⁺	11.4-12.1	H
1,2,3-trimethylbenzene	8.4		No data	
1,2,4-trimethylbenzene	8.3		No data	
Chlorobenzene	9.1	C ₆ H ₅ ⁺		Cl
1,2,-Ddichlorobenzene	9.1	> 12	11.8-13.2	
Esters				
Methyl acetate	10.3	C ₂ H ₂ O ⁺	11.81 ± 0.15	No data
		C ₂ H ₃ O ⁺	10.9-11.4	CH ₃ O
		C ₂ H ₃ O ₂ ⁺	11.3-12.35	CH ₃
Ethyl acetate	10.0	C ₂ H ₃ O ⁺	11.0-11.75	C ₂ H ₅ O
		C ₂ H ₃ O ₂ ⁺	11.74	C ₂ H ₅
		C ₂ H ₄ O ₂ ⁺	11.2 ± 0.1	C ₂ H ₄
		C ₂ H ₅ ⁺	11.3 -12.1	C ₂ H ₃ O ₂
		C ₂ H ₅ O ⁺	10.7-10.8	C ₂ H ₃ O/CH ₃ CO
		C ₂ H ₅ O ₂ ⁺	10.6-11.0	C ₂ H ₃
		C ₃ H ₅ O ₂ ⁺	10.6-11.0	CH ₃

		C ₄ H ₆ O ⁺	10.3 -10.5	H ₂ O
Propyl acetate	9.9	C ₂ H ₅ O ₂ ⁺	9.9-10.5	CH ₂ =CHCH ₂
		C ₃ H ₅ O ₂ ⁺	11.29 ± 0.04	C ₂ H ₅
		C ₃ H ₇ ⁺	11.41 ± 0.04	No data
		C ₃ H ₇ O ⁺	11.64 ± 0.03	CH ₃ CO
Butyl acetate	10.0	C ₃ H ₅ O ₂ ⁺	11.70 ± 0.05	No data
		C ₃ H ₇ ⁺	11.56 ± 0.10	No data
		C ₄ H ₉ ⁺	11.31 ± 0.10	No data
N,N-dimethylformamide	9.1	C ₂ H ₆ N ⁺	11.6	No data
		C ₃ H ₆ NO ⁺	11.35	No data

Table S2. Relative intensities of mass spectrometric components for different VOCs obtained in the current study by pulsed glow discharge time-of-flight mass spectrometry (PGD-TOFMS) and compared to 70 eV electron ionization (EI). For each compound, the highest intensity fragment is taken as 100%.

VOC	Molecular weight, Da	<i>m/z</i>	PGD-TOFMS, relative intensities of ions, %	EI, relative intensities of ions, % [1]
Alkanes				
<i>n</i> -Heptane	100	100	67	15
		71	100	45
		70	35	18
		57	44	47
		56	35	27
		43	13	100
		42	8	25
<i>n</i> -Octane	114	114	21	6
		85	100	26
		71	62	20
		57	33	34
		43	27	100
		41	5	44
		29	3	27
<i>n</i> -Decane	142	142	100	7
		141	71	-
		113	31	5
		99	44	8
		85	67	31
		71	56	44
		57	100	100
		55	71	32
Arenes				
Toluene	92	92	100	78
		91	4	100
		78	1	-
Ethylbenzene	106	106	100	28
		91	100	100
		77	-	10
		65	-	11
		51	-	11

		39	-	7
		106	100	66
<i>p</i> -Xylene	106	91	8	100
		107	10	7
		120	100	45
1,2,4-Trimethylbenzene	120	121	10	4
		119	1	13
		105	2	100
		112	100	100
		114	25	33
		113	4	7
Chlorobenzene	112, 114	115	1	2
		77	-	45
		51	-	12
		50	-	10
Alcohols				
		45	42	51
		43	100	12
Ethanol	46	31	15	100
		29	-	30
		27	-	23
		74	30 (MN ₂ ⁺)	-
		60	2.5	7
		88	68 (MN ₂ ⁺)	-
Propanol-1	60	59	48	12
		58	100	0
		31	34	100
		102	3 (MN ₂ ⁺)	-
		88	55 (MN ⁺)	-
		74	2	14
		71	62	0.2
		58	20	0.8
Isobutanol	74	55	-	10
		43	100	100
		41	3	76
		33	-	32
		31	1	37
		29	-	15
		73	22	1.5
		72	35	-
		56	42	100
Butanol-1	74	43	100	69
		41	-	83
		31	12	98
		27	-	57
		102	84 (MN ₂ ⁺)	-
		87	18	0.75
		85	18	0.1
		105	12 (MOH ⁺)	-
Isoamyl alcohol	88	70	100	70
		58	21	1.5
		57	8	31

		55	11	100
		42	15	85
		39	-	45
		31	4	61
		29	2	60
		27	-	60
Carboxylic acids				
		74	100	100
		57	21	46
		45	5	90
		43	37	6
Propionic acid	74	29	4	85
		28	15	94
		27	-	63
		93	29 (M+H ₃ O ⁺)	-
		104	14 (MNO ⁺)	-
Esters				
		104	60 (MNO ⁺)	-
		93	24 (M+H ₃ O ⁺)	-
		75	100	1
Methyl acetate	74	74	17	25
		61	30	-
		59	-	11
		43	77	100
		29	-	7
		118	56 (MNO ⁺)	-
		107	15 (M+H ₃ O ⁺)	-
		89	100	0.6
		88	16	7
		79	20	-
Ethyl acetate	88	73	1	5
		70	4	12
		61	56	15
		45	16	15
		43	36	100
		29	1	12.5
		146	37 (MNO ⁺)	-
		135	7 (M+H ₃ O ⁺)	-
		117	7	-
		115	2	0.1
		98	4	0.1
Butyl acetate	116	87	4	1.7
		79	31	-
		73	13	18
		61	76	14
		56	100	37
		43	100	100

References:

- [1] Linstrom P J and Mallard W G 2021 NIST Standard Reference Database Number 69. (National Institute of Standards and Technology, Gaithersburg MD p 20899