Electronic Supplementary Information (ESI)

Application of dynamic headspace and gas chromatography coupled to mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery effluents

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S.1 Materials

- Compressed gases: nitrogen, air - purity 5N (Linde Gas, Poland), hydrogen – purity 5.5N from a hydrogen generator (Packard, USA).
- Reagents: carbon disulfide (for GC, Merck, Darmstadt, Germany), acetone (for HPLC, POCH, Poland).
- Standards: alcohols (1-propanol, 2-butanol, 2-methyl-2-butanol, 2-methyl-1-propanol, 1-butanol, 3-pentanol, 3-methyl-1-butanol, 1-pentanol, 1-hexanol, cyclohexanol, benzyl alcohol), aldehydes (acetaldehyde, propionaldehyde, paraldehyde, furfural), ketones (2-butanone, 3-methyl-2-butanone, 2-pentanone, 2-hexanone, cyclopentanone, 2,4-dimethyl-3-pentanone, 3-heptanone, cyclohexanone, 3-methylcyclohexanone), phenols (phenol, o-cresol, m-cresol), esters (ethyl acetate, methyl acrylate, ethyl acrylate, ethyl propionate, isobutyl acetate), ethers (tetrahydrofuran, 2,3-dihydropyran, tetrahydropyran, anisole) (Sigma Aldrich, USA).

S.2 Apparatus

Gas chromatography was performed using an Autosystem XL gas chromatograph with a flame ionization detector (FID), (Perkin Elmer, Waltham, Massachusetts, USA) with a A/C Nelson 900 interface (Perkin Elmer, Waltham, Massachusetts, USA), an Autosystem gas chromatograph with a flame ionization detector (FID) (Perkin Elmer, Clarus 500, USA) with a Nelson NCI 900 interface (Perkin Elmer, USA), a model HP 5890 II gas chromatograph with a model HP 5972A mass spectrometer (Hewlett-Packard, Wilmington, DE, USA), a model G1901-60502 purge and trap concentrator (Hewlett-Packard, Wilmington, DE, USA), capillary columns: DB-624 (60 m x 0.32 mm x 1.80 µm) (Agilent, Santa Clara, CA, USA), HP-5 ms (60 m x 0.25 mm x 0.25 µm) (Agilent, Santa Clara, CA, USA), SLB-IL 111 (30 m x 0.25 mm x 0.2 µm) (Sigma-Aldrich, USA), TurboChrom 6.1 software (Perkin Elmer, USA), Chemstation software (Agilent, USA) and NIST 05 and Wiley 8.0 mass spectra library, a sorbent trap packed with TENAX® (Supelco, USA). COD reactor 45600-00 (HACH, USA), spectrophotometer DR/2010 (HACH, USA), dissolved oxygen sensor COG-1 (ELMETRON, Poland), incubator.

S.3 Procedure

S.3.1 Selection of capillary column for GC-FID

Preparation of standard solutions: Standard solutions of oxygenated volatile organic compounds (O-VOCs) and a mixture of *n*-alkanes were prepared in carbon disulfide at a 100 µg/mL -concentration level.

Chromatographic analysis: Standard solutions were injected directly into the injection port in each of the three chromatographic systems. The injection volume was 1 µL:

- *I system:* - capillary column HP-5ms, - carrier gas: nitrogen at 1 mL/min, split injection (80:1), injection port temperature: 275 °C, detector temperature: 275 °C, FID gases flow rates: air 450 mL/min, hydrogen 40 mL/min, temperature program: 40 °C (5 min) – ramped at 10° C/min -250 °C (10 min).
- *II system:* - capillary column DB-624, - carrier gas: nitrogen at 1.50 mL/min, split injection (80:1), injection port temperature: 220 °C, detector temperature: 220 °C, FID gases flow rates: air 450 mL/min, hydrogen 40 mL/min, temperature program: 40 °C (5 min) – ramped at 10 °C/min -200 °C (10 min).
- *III system:* - capillary column SLB-IL 111, – carrier gas: nitrogen at 1 mL/min, split injection (15:1), injection port temperature: 250 °C, detector temperature: 275 °C, FID gases flow rates: air 450 mL/min, hydrogen 40 mL/min, temperature program: 40 °C (5 min) – ramped at 5 °C/min -220 °C (10 min).

In order to determine the dead time, 0.2 mL of a mixture of methane in nitrogen (*ca*. 100 µg/mL) were injected. Next, retention times of standards were found from the chromatograms and the peaks identified. The data were processed using TurboChrom software and the following parameters computed: retention factor (k'), selectivity factor relative to the preceding compound (α'_1) and selectivity factor relative to *n*-nonane ($\alpha'_{n\text{-}C9}$).

S.3.2 Analysis of real samples

Sample preparation: Samples (2 mL) of raw effluent and treated effluents was transferred to 10-mL vials, which were then capped and placed in the P&T accessory.

Chromatographic analysis: The analysis of effluent samples was carried out using the conditions described in 2.4.2, in SIM and SCAN modes. Three independent determinations were performed for each sample. Analyte identification in SCAN mode was based on comparison of mass spectra of the analytes with those in the NIST and Wiley mass spectra libraries, whereas compounds used for calibration were identified on the basis of two selected ions and retention times of the standards.

S.3.3 Determination of procedure parameters

The limit of detection and quantitation:

The limit of detection (LOD) was calculated from equation (1):

$$\mathrm{LOD} = 3\frac{\mathrm{S}}{\mathrm{N}} \qquad (1)$$

where: S – analyte signal [pA]

N – noise near the analyte retention time [pA].

The limit of quantitation (LOQ) was calculated from equation (2):

$$\mathrm{LOQ} = 2\mathrm{LOD} \qquad (2)$$

Retention factor (k') was calculated from equation (3):

$$\mathrm{k'_i} = \frac{\mathrm{t_{Ri}} - \mathrm{t_0}}{\mathrm{t_0}} \qquad (3)$$

t_{Ri} – retention time [min]

t_0 – dead time [min]

Selectivity factor ($\alpha'_{2\text{-}1}$) was calculated from equation (4):

$$\alpha'_{2-1} = \frac{\mathrm{k'_2}}{\mathrm{k'_1}} \qquad (4)$$

k'_1 - retention factor of compound with a retention time t_{Ri} [-]

k'_2 – retention factor of compound with a dead time t_{Ri+1} [-]

Selectivity factor ($\alpha'_{n\text{-}C9}$) was calculated from equation (5):

$$\alpha'_{n-C9} = \frac{k'_1}{k'_{n-C9}} \qquad (5)$$

$k'_{n\text{-}C9}$ - retention factor of *n*-nonane [-]

Linearity: Linearity was examined in the concentration range described above. Evaluation of linearity of the detector response was based on the correlation coefficient (r), which for the linear relationship between peak area and analyte concentration should be equal to or insignificantly different from 1. The range of linearity of the calibration curve were also determined by standard residual analysis[1] and a simple method, in which for the three independent determinations, for each of the levels of concentration were determined graphic functions from equation (6):

$$\frac{y}{x} = f(x) \qquad (6)$$

y - peak area [Au]

x – concentration of analyte [µg/mL]

On the graph, the value of the constant response was determined as a line parallel to the axis of the abscissa and also lines corresponding 95% confidence level. For the points that were lying outside the accepted values of the confidence level, were labeled as nonlinear points corresponding to the

[1] Huber L., Validation and Qualification in Analytical Laboratories, ISBN 1-57491-080-9, Interpharm Press, Buffalo Grove, 1998.

specified value of the concentration, while points that were within the acceptable range of error was defined as a linear points.

Determination of percent reduction in O-VOC content following effluent treatment using DHS-GC-MS:

Two characteristic m/z values were selected for each of the investigated standards, thus generating the basis for identification of O-VOCs. Chromatographic peaks were integrated based on the signal acquired for the selected ions only. The data obtained in this manner were compared for the examined effluents before and after treatment.

For the chromatographic peaks not belonging to the identification database, identification was further expanded by matching spectra of individual O-VOCs with those in the NIST and Wiley libraries. These compounds were tentatively determined based on the average response factor for a given group of compounds, *i.e.* ketones, aldehydes and alcohols.

S.3.4 Determination of COD, BOD, EC_{20} and EC_{50} parameters.

The basic quality parameters of wastewater - chemical oxygen demand (COD) and biochemical oxygen demand were determined on the basis of standard norms i.e. ISO 15705:2002 and PN/C-04578.05 [2-3].The acute toxicity including EC20 and EC 50 parameters were determined by Microtox test on the basis of the EN ISO 11348-3:1998 norm [4].

S.4 Results

S.4.1 Selection of capillary column

In order to optimize chromatographic separation of 36 O-VOC compounds, the standard solution was chromatographed using three capillary columns with various polarities. The retention times for individual compounds along with their peak numbers and selectivity factors with respect to the preceding compound and *n*-nonane are compiled in Tables S1, S2 and S3. This hydrocarbon was selected due to the fact that for the most polar stationary phase (IL-111) lower *n*-alkanes were eluted at the dead time.

[2] ISO 15705:2002 Water quality - Determination of the chemical oxygen demand index (ST-COD) - Small-scale sealed-tube method.

[3] PN/C-04578.05 Test for oxygen demand and organic carbon content. Determination of biochemical oxygen demand (BODn) by the dilution method.

[4] EN ISO 11348-3:1998 Water quality - Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test) -- Part 3: Method using freeze-dried bacteria.

A nonpolar HP-5ms column with the 5% phenyl – 95% dimethylpolysiloxane stationary phase yielded the poorest separation. In addition, acetaldehyde and propionaldehyde were eluted at the dead time (Figure S2). The column with a nonpolar stationary phase, such as HP – 5ms, is characterized by the insufficient selectivity. The elution order and retention are determined solely by dispersive interactions while dipole-dipole interactions and hydrogen bonding are absent, so that they do not affect retention.

The use of a moderately polar DB-624 column with the 6% cyanopropyl-phenyl-94% dimethylpolysiloxane stationary phase (Figure S3) resulted in coelution of several pairs of compounds or incomplete resolution of some chromatographic peaks. The following compounds were coeluted: tetrahydropyran, furfural and ethyl propionate; 2,4-dimethyl-3-pentanone and 3-methyl-2-butanone as well as anisole and cyclohexanol. Similarly to the nonpolar column, acetaldehyde and propionaldehyde were eluted at the dead time. The elution order of compounds within a homologous series was determined primarily by their boiling point, which resulted in a high selectivity of the column for compounds with a large difference in polarity. This phenomenon is caused by the presence of cyanopropyl and phenyl groups on the surface of the stationary phase, resulting in strong dispersive interactions. In addition, the cyanopropyl group exhibits strong dipole-dipole interactions providing selectivity of the stationary phase for a number of groups of polar analytes relative to *n*-alkanes.

The most polar column SLB-IL 111 with the stationary phase being an ionic liquid (1,5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide) (Figure 1) had the highest selectivity towards the standard mixture. Coelution was observed only for a few compounds, such as 3-pentanol and 2-pentanone as well as 2,4-dimethyl-3-pentanone and 3-heptanone. At the same time, small values of the selectivity factor (α'_1) were found for several pairs of compounds, *i.e.* 2-butanone and ethyl acrylate as well as 1-propanol and paraldehyde. The SLB-IL 111 column is characterized by strong dispersive and dipole-dipole interactions, which mainly determine the elution order of analytes. Hydrogen bonding on the surface of the stationary phase plays a minor role. Hydrogen bonding has a significant effect on retention of only some groups of compounds, *i.e.* alcohols, which can form a hydrogen bond with the stationary phase both through a hydrogen atom and through the lone electron pair on oxygen. For ketones, esters and aldehydes, only the latter type of hydrogen bond is possible.

On the basis of the results obtained, the SLB-IL111 column with the ionic liquid stationary phase was selected for further work, since it ensures the highest selectivity towards O-VOC compounds, as demonstrated by the selectivity factors relative to the preceding compound (Figure S4). The few coelutions should not interfere with the procedures making use of GC-MS due to substantial differences in mass spectra of the separated compounds and the occurrence of numerous specific

fragmentation ions. Furthermore, previous investigations [7,11,15] revealed that the samples of postoxidative effluents contain *n*-alkanes, which under the DHS conditions are released in the *n*-C5 to *n*-C9 range with small amounts of *n*-C10 do *n*-C13 also present. Under the selected separation conditions *n*-alkanes up to n-C8 are eluted at the dead time; thus, the use of IL-111 column largely reduces the matrix effect.

S.4.2 Results of analysis

Among the compounds identified in raw effluent there is just one ester – ethyl acrylate at a concentration of 0.11 µg/mL. On the other hand, 2,3-dihydropyran, an ether, is present in all of the investigated samples except for those that were treated by ozonation. In all the remaining cases, a slight decrease in concentration of 2,3-dihydropyran was observed. This is due to low reactivity of ethers associated with the presence of the stable bond C-O-C. Ethers can be oxidized by oxygen and ozone, which initiate a radical reaction with the insertion of oxygen molecule, breaking the C-H bond at the carbon bonded to oxygen, and the formation of hydroperoxides of ethers. Only one aldehyde, furfural, was present in all the effluent samples. Studied treatments lowered this value.

A substantial reduction in the content of aliphatic ketones is observed only for the effluent samples treated by ozonation. In the samples treated by sono-cavitation with additional oxidants analytical increase in concentration of these compounds was observed. The content of cyclic ketones, i.e. cyclohexanone and 3-methylcyclohexanone also increased in comparison with raw effluents. A summary of the results is shown in Table 2.

A comparison of the content of individual compounds in raw effluent with that in chemically treated effluent reveals that sono-cavitation with hydrogen peroxide and ozone result in an increase in O-VOCs content. The content of the majority of the compounds was either completely or largely removed following ozonation of the effluents. To a large extent, this can be due to the purging effect of a strongly dispersed stream of gas, removing a fraction of the VOCs from the liquid by their partitioning between the two phases. The extent of the purging increases with the vapor pressure (volatility) of volatile organic compounds present in effluents.

Table S1. Compilation of standard compounds along with their retention times and corresponding numbers in chromatograms for the tested column (HP-5ms) as well as the experimental selectivity factors (α'_{1} and $\alpha'_{n\text{-}C9}$).

No.	Compound	t_R [min]	k'	$\alpha'_{2\text{-}1}$	$\alpha'_{n\text{-}C9}$
1	Acetaldehyde	4.78	0.04	-	0.02
2	Propionaldehyde	5.06	0.10	2.40	0.05
3	1-propanol	5.82	0.27	2.58	0.14
4	2-Butanol	6.51	0.42	1.56	0.22
5	2-butanone	6.51	0.42	1.00	0.22
6	Ethyl acetate	6.82	0.49	1.16	0.26
7	Methyl acrylate	6.83	0.49	1.00	0.26
8	2-Methyl-1-propanol	7.03	0.53	1.09	0.28
9	Tetrahydrofuran	7.08	0.55	1.02	0.29
10	2-Methyl-2-butanol	7.27	0.59	1.08	0.31
11	1-Butanol	7.76	0.69	1.18	0.36
12	2-Pentanone	8.26	0.80	1.16	0.42
13	2.3-dihydropyran	8.42	0.84	1.04	0.44
14	Ethyl acrylate	8.55	0.87	1.03	0.45
15	3-Pentanol	8.56	0.87	1.00	0.45
16	Tetrahydropyran	8.76	0.91	1.05	0.48
17	Ethyl propionate	8.89	0.94	1.03	0.49
18	3-Methyl-1-butanol	9.43	1.06	1.13	0.55
19	1-Pentanol	10.28	1.24	1.18	0.65
20	Isobutyl acetate	10.42	1.28	1.02	0.67
21	3-Methyl-2-butanone	10.62	1.32	1.03	0.69
22	Paraldehyde	10.69	1.33	1.01	0.70
23	2-Hexanone	10.81	1.36	1.02	0.71
24	Cyclopentanone	10.84	1.37	1.00	0.72
25	2.4-Dimethyl-3-pentanone	10.91	1.38	1.01	0.72
26	Furfural	11.83	1.58	1.15	0.83
27	1-Hexanol	12.71	1.78	1.12	0.93
28	3-Heptanone	13.05	1.85	1.04	0.97
29	Cyclohexanol	13.14	1.87	1.01	0.98
30	Cyclohexanone	13.31	1.91	1.02	1.00
31	Anisole	13.82	2.02	1.06	1.06
32	3-Methylcyclohexanone	14.57	2.18	1.08	1.14
33	Phenol	15.02	2.28	1.05	1.19
34	Benzyl alcohol	16.14	2.52	1.11	1.32
35	o-cresol	16.43	2.59	1.03	1.35
36	m-cresol	16.77	2.66	1.03	1.39

(Dead time: 4.58 min; retention time of n-nonane: 13.35 min, k'=1.91).

Table S2. Compilation of standard compounds along with their retention times and corresponding numbers in chromatograms for the tested column (DB-624) as well as the experimental selectivity factors (α'_1 and $\alpha'_{n\text{-}C9}$).

No.	Compound	t_R [min]	k'	$\alpha'_{2\text{-}1}$	$\alpha'_{n\text{-}C9}$
1	Acetaldehyde	6.10	0.42	-	0.19
2	Propionaldehyde	8.62	1.01	2.39	0.44
3	1-propanol	10.93	1.55	1.53	0.68
4	2-butanone	11.78	1.75	1.13	0.77
6	Ethyl acetate	11.87	1.77	1.01	0.78
7	Methyl acrylate	11.96	1.79	1.01	0.79
5	2-Butanol	12.01	1.80	1.01	0.79
9	Tetrahydrofuran	12.30	1.87	1.04	0.82
8	2-Methyl-1-propanol	12.85	2.00	1.07	0.88
10	2-Methyl-2-butanol	13.03	2.04	1.02	0.90
21	3-Methyl-2-butanone	13.50	2.15	1.05	0.95
11	1-Butanol	13.78	2.21	1.03	0.97
13	2.3-dihydropyran	13.91	2.24	1.01	0.99
14	Ethyl acrylate	14.13	2.29	1.02	1.01
12	2-Pentanone	14.21	2.31	1.01	1.02
16	Tetrahydropyran	14.36	2.35	1.02	1.03
26	Furfural	14.38	2.35	1.00	1.04
17	Ethyl propionate	14.40	2.36	1.00	1.04
15	3-Pentanol	14.56	2.39	1.02	1.05
22	Paraldehyde	15.39	2.59	1.08	1.14
18	3-Methyl-1-butanol	15.54	2.62	1.01	1.16
20	Isobutyl acetate	15.97	2.72	1.04	1.20
19	1-Pentanol	16.27	2.79	1.03	1.23
25	2.4-Dimethyl-3-pentanone	16.65	2.88	1.03	1.27
23	2-Hexanone	16.73	2.90	1.01	1.28
24	Cyclopentanone	17.11	2.99	1.03	1.32
27	1-Hexanol	18.43	3.30	1.10	1.45
28	3-Heptanone	18.66	3.35	1.02	1.48
29	Cyclohexanol	19.06	3.44	1.03	1.52
31	Anisole	19.42	3.53	1.02	1.55
30	Cyclohexanone	19.47	3.54	1.00	1.56
32	3-Methylcyclohexanone	20.63	3.81	1.08	1.68
33	Phenol	21.75	4.07	1.07	1.79
34	Benzyl alcohol	22.36	4.21	1.03	1.86
35	o-cresol	23.00	4.36	1.04	1.92
36	m-cresol	23.66	4.52	1.04	1.99

(Dead time: 4.29 min; retention time of n-nonane: 15.96 min, k'=2.27).

Table S3. Compilation of standard compounds along with their retention times and corresponding numbers in chromatograms for the tested column (SLB-IL 111) as well as the experimental selectivity factors (α'_1 and $\alpha'_{n\text{-}C9}$).

No.	Compound	t_R [min]	k'	$\alpha'_{2\text{-}1}$	$\alpha'_{n\text{-}C9}$
1	Acetaldehyde	3.81	0.15	-	1.89
2	Propionaldehyde	4.33	0.31	2.04	3.85
9	Tetrahydrofuran	4.79	0.45	1.45	5.59
13	2.3-dihydropyran	5.28	0.60	1.33	7.44
16	Tetrahydropyran	5.34	0.61	1.03	7.67
6	Ethyl acetate	5.75	0.74	1.20	9.21
7	Methyl acrylate	6.30	0.90	1.23	11.29
5	2-Butanol	6.54	0.98	1.08	12.20
10	2-Methyl-2-butanol	6.63	1.00	1.03	12.54
17	Ethyl propionate	6.75	1.04	1.04	12.99
4	2-butanone	7.33	1.21	1.17	15.18
14	Ethyl acrylate	7.34	1.22	1.00	15.22
21	3-Methyl-2-butanone	7.69	1.32	1.09	16.54
8	2-Methyl-1-propanol	8.36	1.53	1.15	19.07
20	Isobutyl acetate	8.56	1.59	1.04	19.83
3	1-propanol	8.81	1.66	1.05	20.77
22	Paraldehyde	8.82	1.66	1.00	20.81
15	3-Pentanol	10.17	2.07	1.25	25.91
12	2-Pentanone	10.17	2.07	1.00	25.91
11	1-Butanol	11.24	2.40	1.16	29.95
18	3-Methyl-1-butanol	11.50	2.47	1.03	30.93
23	2-Hexanone	12.21	2.69	1.09	33.61
19	1-Pentanol	12.83	2.88	1.07	35.95
28	3-Heptanone	14.19	3.29	1.14	41.09
25	2.4-Dimethyl-3-pentanone	14.22	3.30	1.00	41.20
24	Cyclopentanone	16.43	3.96	1.20	49.55
29	Cyclohexanol	16.51	3.99	1.01	49.85
27	1-Hexanol	16.64	4.03	1.01	50.34
31	Anisole	16.93	4.12	1.02	51.44
30	Cyclohexanone	18.49	4.59	1.11	57.33
32	3-Methylcyclohexanone	19.60	4.92	1.07	61.52
26	Furfural	22.75	5.87	1.19	73.41
34	Benzyl alcohol	30.12	8.10	1.38	101.25
35	o-cresol	31.00	8.37	1.03	104.57
33	Phenol	31.95	8.65	1.03	108.16
36	m-cresol	33.73	9.19	1.06	114.88

(Dead time: 3.31 min; retention time of n-nonane: 3.57 min., k'=0.08).

Table S4. Compilation of average (n=3) signal-to-noise ratio values (S/N) for standard compounds at a concentration of 50 µg/mL in split, splitless (1.0 ; 1.2) and splitless (3.8 ; 4.0) modes

No.	Compound	S/N		
		Split	Splitless (1.0 ; 1.2)	Splitless (3.8 ; 4.0)
1.	anisole	1372.6	1121.9	1051.0
2.	cyclohexanone	93.6	44.8	69.8
3.	3-methylcyclohexanone	69.3	36.0	49.3
4.	furfural	72.8	51.2	66.8
5.	benzyl alcohol	38.2	21.9	28.2

Table S5. Compilation of identified compounds in samples of raw postoxidative effluents and chemically treated effluents using SCAN mode along with retention times, characteristic ions and estimated concentrations

No.	Name	t_R [min]	m/z_{id}	m/z_{int}	Concentration [µg/mL]		
					Raw effluent	Effluent I	Effluent II
1.	2-propanol	1.68	45	43	3 979.07	5 374.51	82.39
2.	acetone	1.84	43	58	1 924.41	6 129.01	66.77
3.	pentaldehyde	2.13	44	86	203.97	358.85	-
4.	3-methylbutanal	2.64	86	71	92.97	112.86	-
5.	2-penten-1-ol	3.08	57	86	214.65	206.85	-
6.	hexanal	3.71	56	72	321.05	387.57	-
7.	octanal	4.27	43	57	155.09	513.10	-
8.	1,2-cyclopentanediol	5.24	55	84	80.99*	49.63	-
9.	3-hydroxybutanal	7.78	70	71	49.41	22.51	-

Averaged parameters of calibration curves for individual groups of compounds:

Aldehydes: a =1311 b = 1087 (n=2, Sa=196 Sb=5)

Ketones: a = 14484 b = 1685 (n=4 Sa=1685 Sb=828)

Alcohols: a = 1570 b = 1285 (n=5 Sa=446 Sb=173)

** The difference in ratio of m/z_{id} to m/z_{int} for raw effluent is within 10 to 20% of the value established during identification. For the remaining compounds, the difference in m/z_{id} to m/z_{int} ratio does not exceed 10% of the value.*

Table S6 Compilation of COD, BOD, EC20 and E50 test results.

Parameter	Raw effluent	Effluent I	Effluent II
COD [mgO_2/L]	7575	3775	6025
BOD [mgO_2/L]	2400	1100	1700
EC_{20} [%]	0.1	1	0.7
EC_{50} [%]	0.6	5.5	2.4

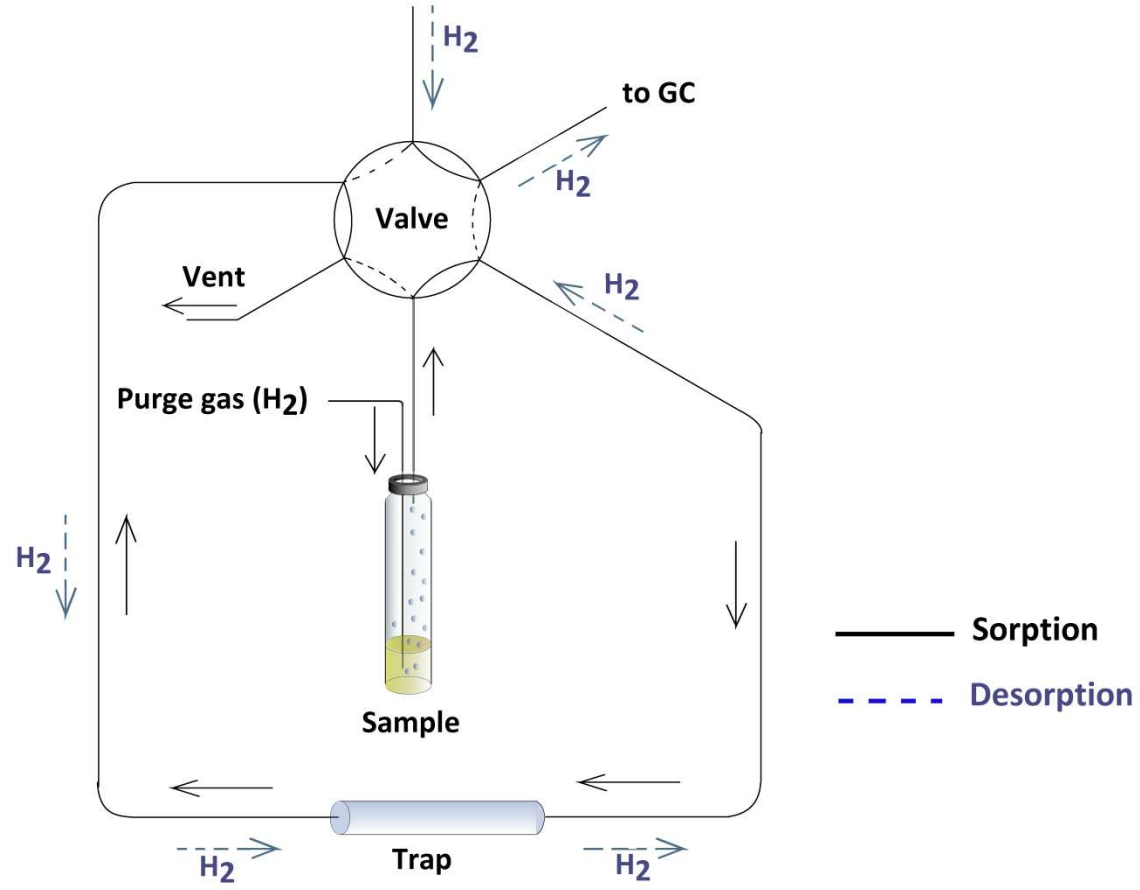

Fig. S1 Schematic diagram of a purge-and-trap system (P&T).

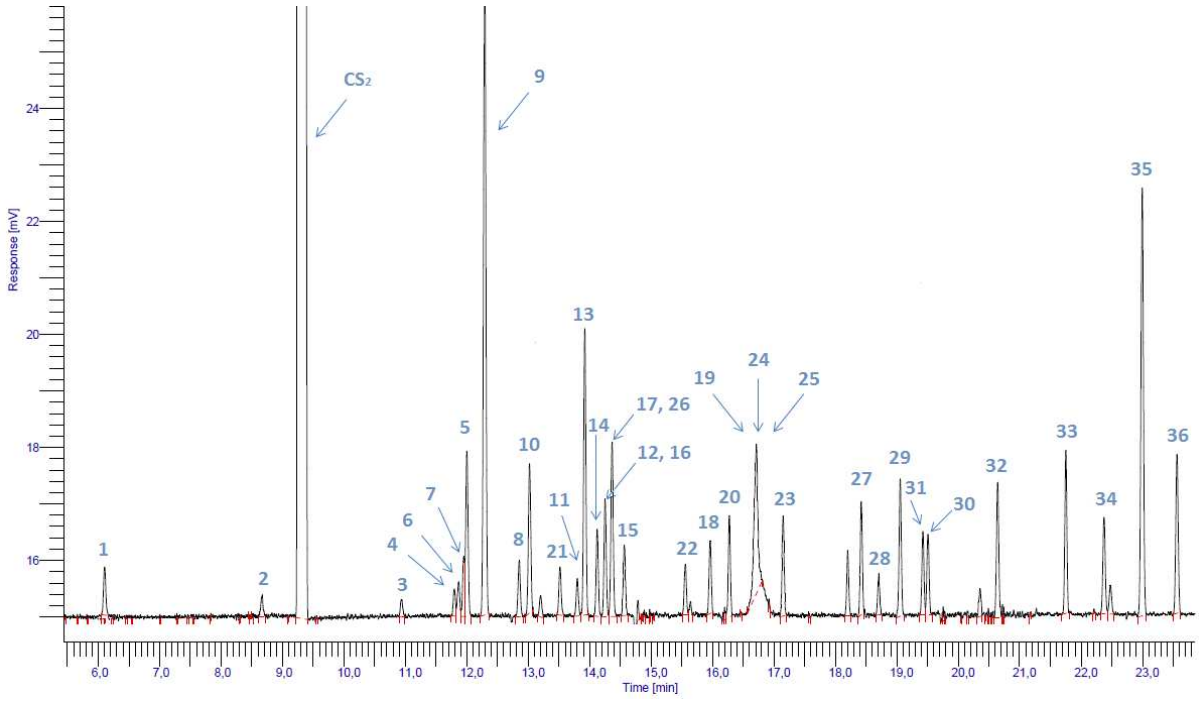

Fig. S2 Chromatogram of a mixture of standards of alcohols, ketones, aldehydes, phenols, esters and ethers separated on a HP-5 ms column

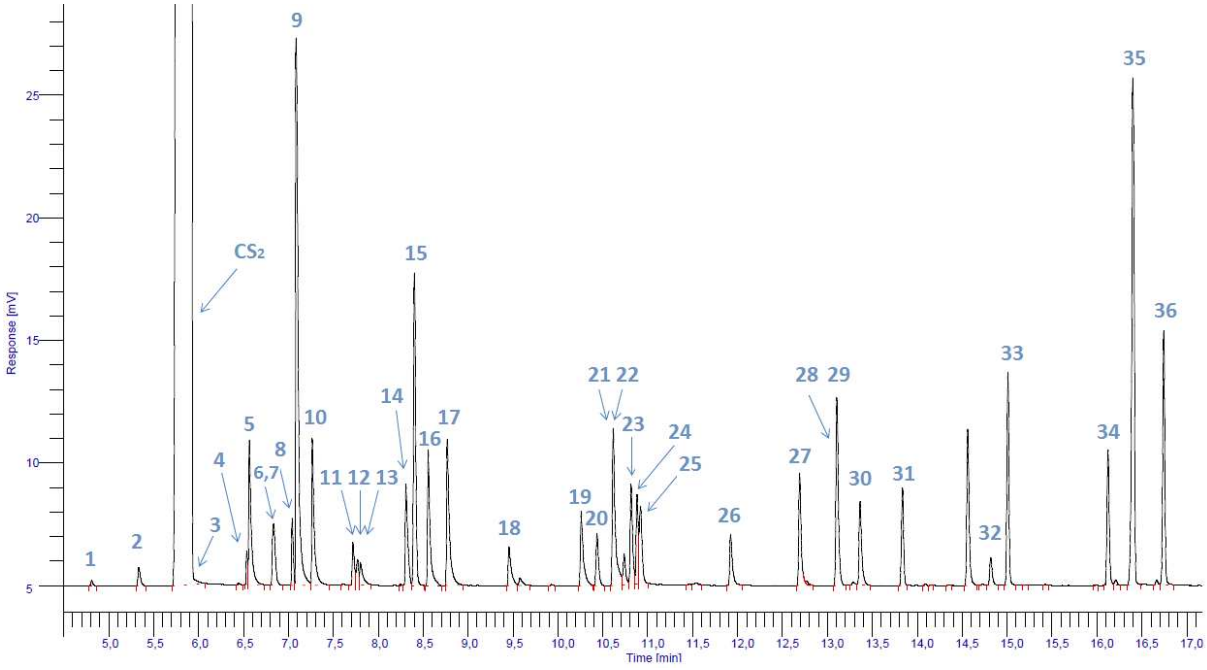

Fig. S3 Chromatogram of a mixture of standards of alcohols, ketones, aldehydes, phenols, esters and ethers separated on a DB-624 column

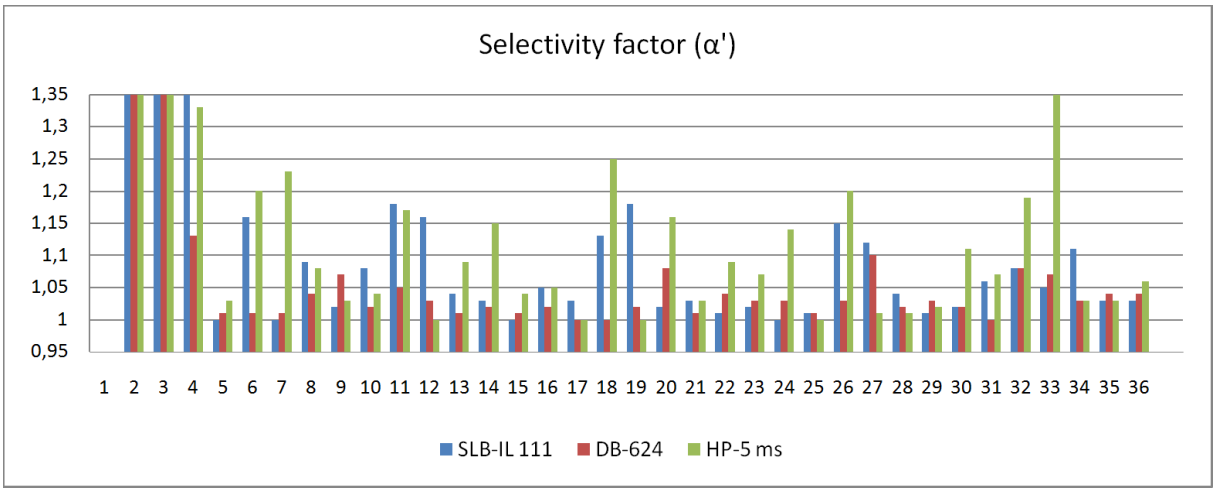

Fig. S4 Plot of selectivity factor with respect to the preceding compound for the examined columns

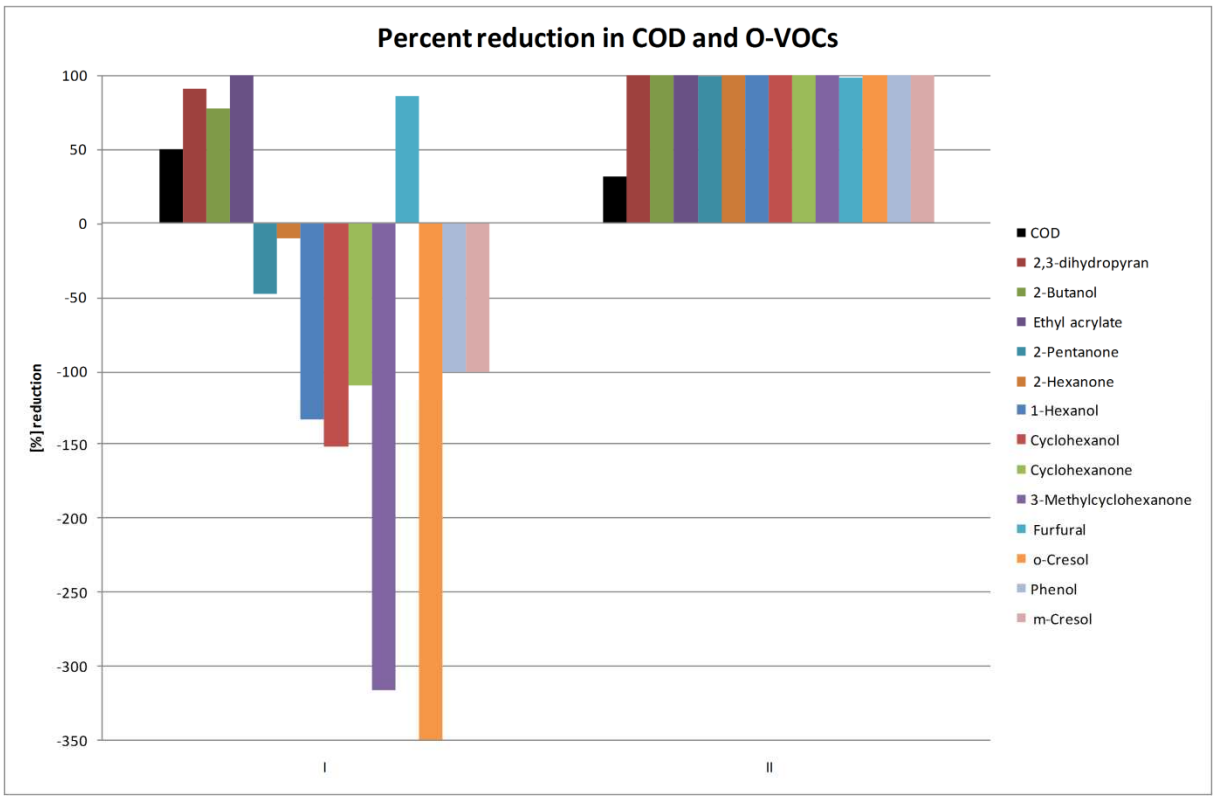

Fig. S5 Percent reduction in O-VOC content and COD values following chemical treatment of raw effluents. Reduction in content is represented by positive % values.