Electronic Supplementary Information

Corona Discharge Radical Emission Spectroscopy: A Multi-channel Detector with Nose-type Function for Discrimination Analysis

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Fabrication of the Corona Discharge System

The instrumental set-up for corona discharge is schematically described in Figure S1. A quartz tube was employed as the discharge tube. Two Pt/Ir needle electrodes (the tips were simply prepared by cutting Pt/Ir wire with a pair of scissors, and the diameter of the tips is 0.3 mm) were inserted into the quartz tube for discharge, while another two tubules for gas in and out, were located at the middle of the quartz tube perpendicular to the electrodes. The power supply for the corona discharge is composed of a regulator (TDGC-1KVA, Shanghai People Electromechanical Equipment Ltd. Co., Shanghai, China) and an ozone generation power supply (YG.BP102P, Electronic Equipment Factory of Guangzhou Salvage, Guangzhou, China). Samples were manually injected into a tight-sealed bottle (volume: 50 mL) and vaporized at appropriate temperature. Then they were delivered into the quartz glass tube with Ar gas, where they were dissociated by the corona discharge between the electrodes. Emission from the discharge was collected with a CCD spectrometer (Maya 2000 PRO, Ocean Optics Inc., Dunedin, FL, USA). Optimized operation parameters: voltage on electrodes, ~1500 V; Ar flow rate, 0.6 L min^{-1}; samples volume, 1 μL; the distance between the two electrodes, ~0.5 mm; vaporization time, 30 s; vaporization temperature, 503 K; and CCD signal integration time: 100 ms. For convenience of explanation, the concentration of the analyte is defined as V (analyte)/V (vaporization bottle). Accordingly, all sample concentrations were 0.02 μL mL^{-1} (ppmv).

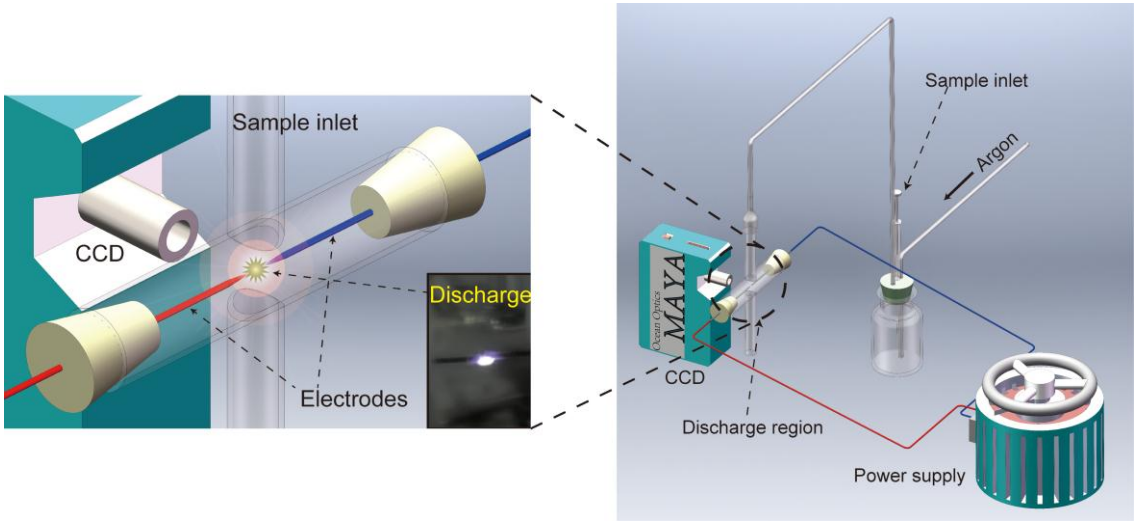


Figure S1 Structure of the corona discharge and the optical arrangement for detection.

Spectral Characteristics

In order to better understand the dissociation process, the broad emission spectra of ethanol was acquired by using two CCD spectrometers with complementary wavelength ranges (the two Ocean Optics CCD spectrometers' wavelength ranges were customized to 200-401 nm and 395-590 nm). The combined emission spectra from the two CCD spectrometers was given in Figure S2. One can see that, at least 4 kinds of radicals, i.e., OH, CN, CH and C_2, could be identified, which originate from the dissociation of sample molecules and intermediates reactions. The formation of CN radical was speculated from the interaction between samples and trace N_2 in the Ar carrier gas. In our experiments, since the carrier gas Ar was continuously and constantly delivered, the N_2 concentration in Ar should be constant. Thus, the peak intensity of CN actually reflected the scale of the interaction between sample molecules and N_2 molecules Accordingly, the CN emission peak (421.7 nm) was also selected for quantification.

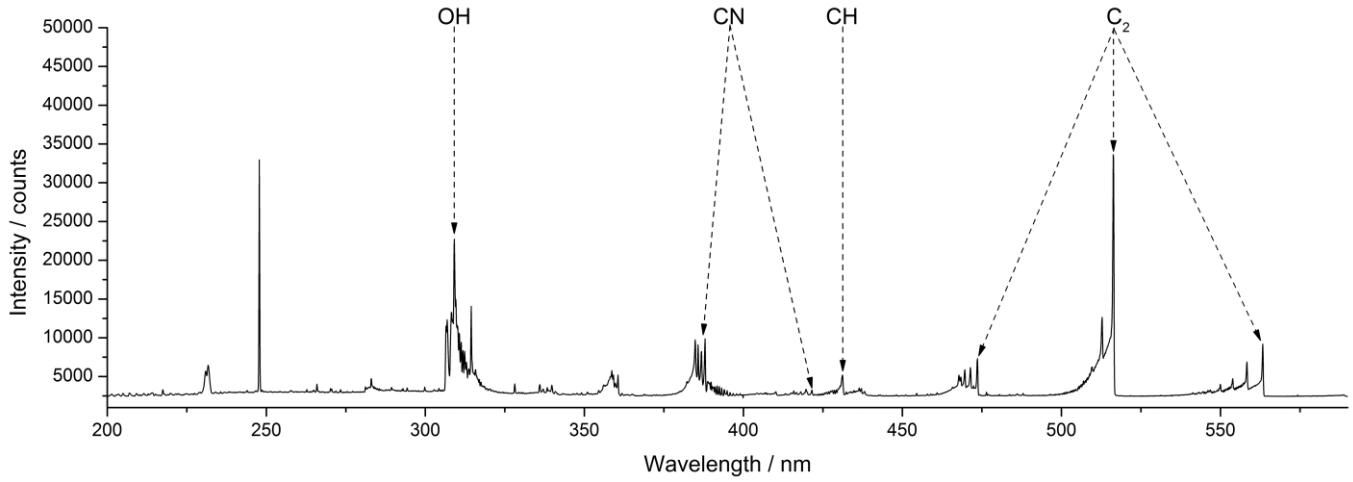


Figure S2 Emission spectra of ethanol in the wavelength region of 200-590 nm.

For LDA, the area intensities were obtained by subtracting the background from the integrated peak (Figure S3). In experimental operations, the different peak widths of various VOCs were taken into consideration. That is, we waited for the emission peak returned to baseline to make ready for next injection. The peak areas of 421.7, 431.3, 512.9, 516.5 and 563.4 nm in one test were named a group of intensity data.

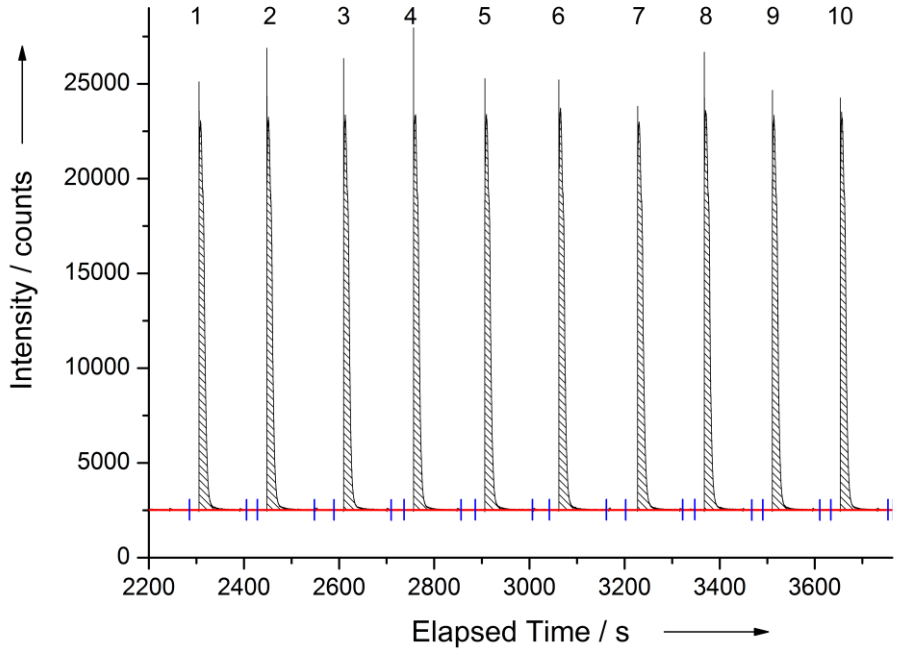


Figure S3 An example for peak area calculation schemes (ethanol, 516.5 nm). The red line is defined as the baseline. Peak area is obtained by subtraction of integrated baseline area (without injection) from that of the whole peak area (integration range: between two blue short lines that enclose the peak area).

Limits of Detection

The limits of detection (LOD) for each analyte were evaluated based on the 3σ criterion. Generally, the theoretical LODs for these VOCs are in the range of 0.2-20 ppbv. However, when the concentrations of these VOCs were lower than 20 ppbv, the RES signal is relatively unstable, with typical RSD for triplicate measurements higher than 5%. Thus,

from analytical point of view, we think 20 ppbv may be the lowest concentration for such system to obtain reliable signals, i.e., the LODs for recognition analysis are 20 ppbv.

Response Time

For the response time, the dead time (from sample injection to analyte appeared in the plasma) is identical for all VOCs, since the temperature of the vaporization bottle is higher than the vaporization temperatures of all VOCs. Accordingly, here we defined response time as the time of intensity reach the highest point from the 10% peak height point. The response time, full width at half maximum (FWHM) and boiling point of the eight VOCs are listed in Table S1. Unlike the response times, FWHMs have a narrow distribution and are approximately proportionally correlated with the boiling point. Considering thermal evaporation being used for sample introduction, thermal properties of analytes may be an important influencing factor to the response times and FWHMs. When the gaseous analytes go through the gas pipe, their temperatures will decrease and the analytes convert to liquid partly. The analytes with high boiling temperatures will need more time to pass the pipe. Different from FWHM, response time is determined by the appearance of maximum mainly and the probable influencing factors may include analytes' boiling point, adsorption/desorption in the gas pipe, dissociation mechanism and efficiency of discharge dissociation, etc. The cause of wide distribution of response times is not very clear yet. The analytes with low boiling point, poor stability, low adsorption in the gas pipe and easy dissociation in the corona discharge can reach the peak value in a shorter time.

Table S1. Response times of eight VOCs.

Analyte	Response Time (s)	FWHM (s)	Boiling Point (K)
Acetone	2.7	10.1	329.7
Methanol	2.5	9.8	338.6
Ethyl acetate	0.2	12.0	350.2
Ethanol	0.2	11.3	351.5
Butanone	5.5	10.1	352.8
Formic acid	9.9	12.7	374.0
Acetic acid	0.4	12.9	391.1
Butyl acetate	0.4	16.6	399.3

Understanding the Mechanism from Bond Dissociation Energy

It is known that the dissociation processes of a given molecule are largely associated with the bond dissociation energy (BDE). Here the BDEs of isomers were calculated to explain the effect of the structure influences on dissociation processes (Table S2). All optimisations and frequency calculations were performed using Gaussian at the B3LYP/6-311++ G** level of theory. BDEs were obtained by calculating the enthalpy changes before and after reaction.[1] Based on the calculation results, it is evident that the oxygen atoms have significant influences on the BDEs of adjacent C-C and C-H bonds. Due to the different BDEs, these isomers will undergo different dissociation pathways in the corona discharge, leading to ultimate discrimination of these isomers in CDRES.

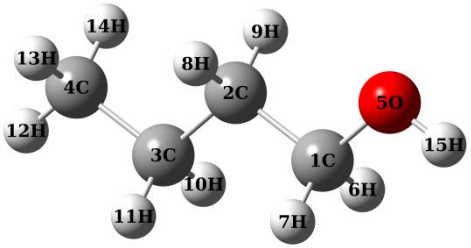
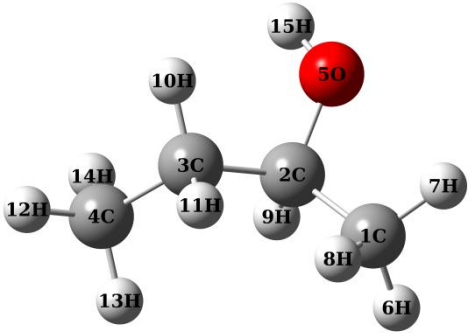
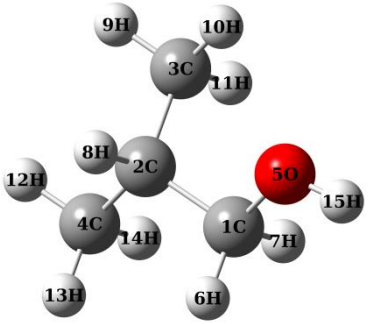
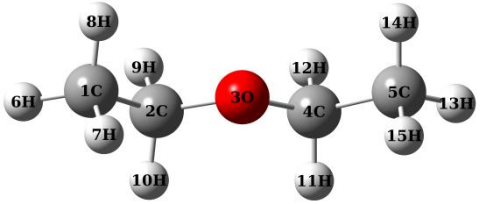
Analyte	1-Butanol		2-Butanol		Isobutanol		Ether	
Molecular structure								
Bond	Dissociation site	BDE (kJ mol^{-1})	Dissociation site	BDE (kJ mol^{-1})	Dissociation site	BDE (kJ mol^{-1})	Dissociation site	BDE (kJ mol^{-1})
C-H	1C-6H 1C-7H 2C-8H 2C-9H 3C-10H 3C-11H 4C-12H 4C-13H 4C-14H	382.1 382.1 402.3 402.3 396.9 396.9 412.5 413.1 413.1	1C-6H 1C-7H 1C-8H 2C-9H 3C-10H 3C-11H 4C-12H 4C-13H 4C-14H	416.4 418.1 416.4 376.5 396.4 396.4 411.6 411.3 407.5	1C-6H 1C-7H 2C-8H 3C-9H 3C-10H 3C-11H 4C-12H 4C-13H 4C-14H	383.9 383.6 389.5 414.3 414.3 414.3 413.7 413.7 413.7	1C-6H 1C-7H 1C-8H 2C-9H 2C-10H 4C-11H 4C-12H 5C-13H 5C-14H 5C-15H	420.6 417.5 417.5 381.9 381.9 381.9 381.9 420.6 417.5 417.5
C-C	1C-2C 2C-3C 3C-4C	338.3 335.9 340.6	1C-2C 2C-3C 3C-4C	325.7 310.1 341.4	1C-2C 2C-3C 2C-4C	324.2 334.7 335.1	1C-2C 3C-4C	333.3 333.3
C-O	1C-5O	364.3	2C-5O	360.5	1C-5O	364.5	2C-3O 4C-3O	311.7 311.7
O-H	5O-15H	409.3	5O-15H	414.4	5O-15H	411.5		

Table S2. Molecular structures and BDEs of four isomers calculated using Gaussian

Linear Discrimination Analysis

For constructing the training matrix, each of the eight VOCs was repeatedly injected 10 times. Thus, a 8 (number of VOCs) × 5 (number of wavelengths) × 10 (repeated times) matrix were generated (Table S4). Meanwhile, 160 unknowns were randomly prepared and subjected to CDRES analysis (Table S5). LDA classified the training matrix and predicted testing matrix. The standardized canonical scores of each peak on the first two factors were listed in Table S3. Obviously, the emission peaks of 512.9 and 516.5 nm have large scores, which reflects that C_2 radical generate processes vary greatly between analytes. The classification data and corresponding canonical scores for wines and isomers are tabulated in Table S6 and Table S7, respectively.

Table S3. Standardized canonical weights of every peak on the first two factors.

Peak	Factor 1	Factor 2
421.7 nm	0.6562	0.44973
431.3 nm	-0.14212	-1.76915
512.9 nm	-9.60496	6.14322
516.5 nm	8.60209	-8.54951
563.4 nm	1.69004	3.89191

Table S4. Training matrix for LDA of volatile organic compounds.

Sample	Intensity (peak area)					Canonical Score	
	421.7 nm	431.3 nm	512.9 nm	516.5 nm	563.4 nm	Factor (1)	Factor (2)
Acetone	29930.6	95002.9	176854.3	398304.4	105977.7	27.02765	19.48752
Acetone	30239.0	92817.7	168343.9	379684.0	100816.6	25.33015	17.73913
Acetone	31019.4	95759.6	178596.2	402126.6	106888.2	28.61674	20.16786
Acetone	30492.1	94454.0	175089.4	395224.0	104887.8	28.20618	18.65404
Acetone	29572.0	91017.3	170379.6	384744.8	101907.6	25.81517	18.98745
Acetone	30286.8	92761.2	173890.5	392008.4	103809.3	26.75049	19.58484
Acetone	30186.3	94457.6	169601.1	382378.9	101650.7	25.46259	16.87829
Acetone	30722.2	92536.5	170447.7	384353.6	101711.8	26.22771	18.59537
Acetone	30291.3	88486.4	160701.2	362705.6	96461.6	23.66864	19.25758
Acetone	30974.0	95432.5	178034.0	401219.8	106020.3	28.35832	18.70795
Butanone	33070.4	100244.6	199863.8	447569.9	120898.6	36.01043	31.44693
Butanone	35115.2	101715.4	200941.0	449523.5	121330.3	37.94709	32.20693
Butanone	34447.8	104362.7	206632.3	461753.3	124615.3	38.01447	31.72423
Butanone	34296.1	104665.4	213415.1	475975.0	128260.2	38.4306	34.42156
Butanone	35871.4	101287.3	201220.3	450416.4	121939.7	39.69831	33.96881
Butanone	35470.4	108099.3	210189.1	468922.8	126567.7	38.95602	30.86927
Butanone	33723.0	104343.1	212043.3	472983.2	127431.5	37.42045	33.59178
Butanone	34124.6	104683.9	207365.7	463491.5	124905.0	37.81593	31.01637
Butanone	33721.3	104081.4	211601.7	472388.7	127221.3	37.82332	33.3091
Butanone	34427.9	107101.6	214159.3	477786.3	128655.0	38.75807	32.10545
Methanol	9019.6	37652.6	12803.8	31235.8	8911.0	-44.37634	-6.22833
Methanol	8959.0	37187.6	12623.2	30760.8	8760.3	-44.59245	-5.88746
Methanol	8838.3	37497.0	12847.8	31234.0	8940.9	-44.68543	-6.07474
Methanol	9016.9	38653.6	13552.5	33027.3	9436.3	-44.01434	-6.90656
Methanol	8935.4	38147.7	12937.3	31407.5	9039.3	-44.58538	-6.48869
Methanol	9227.4	37251.3	12228.4	29773.6	8516.7	-44.532	-5.78668
Methanol	8832.1	36651.2	12294.3	29888.5	8529.4	-45.00058	-5.49576
Methanol	8898.2	36959.5	12469.7	30169.5	8664.0	-44.9986	-5.48396
Methanol	8797.2	36836.2	12480.1	30317.3	8621.4	-45.00036	-5.68844
Methanol	9082.9	38123.5	13072.8	31687.5	9095.8	-44.41339	-6.30884
Formic acid	2168.6	9236.9	1699.3	2866.9	643.5	-59.52502	13.01491
Formic acid	2109.6	8811.7	1671.4	2871.7	689.2	-59.43315	13.4313
Formic acid	2257.2	9075.4	1641.6	2864.7	673.1	-59.21313	13.20653
Formic acid	2175.4	8951.8	1623.0	2859.0	678.1	-59.24944	13.24594
Formic acid	2147.2	8620.7	1625.5	2838.1	695.8	-59.2732	13.62306
Formic acid	2258.6	8956.8	1708.2	3028.9	728.7	-59.14819	13.36933
Formic acid	2340.3	9152.4	1794.2	3030.8	818.1	-59.23467	13.58201
Formic acid	2410.8	9203.7	1727.8	2935.6	756.7	-59.13004	13.45197
Formic acid	2377.3	9152.1	1747.8	2997.4	783.1	-59.12637	13.49415
Formic acid	2505.6	9255.8	1823.7	3157.0	813.6	-58.9823	13.50844
Ethanol	20822.6	70143.3	109411.6	251885.5	66907.0	3.32429	6.12705
Ethanol	19667.2	68019.6	107658.1	247122.0	65514.2	0.23171	6.88258
Ethanol	19819.3	67837.1	108621.8	248822.5	66176.7	0.2608	8.31871
Ethanol	19582.6	67203.9	107488.3	246699.2	65439.6	0.11497	7.67147
Ethanol	19884.9	69172.2	110017.5	251866.0	66996.4	0.56361	7.67344
Ethanol	19436.5	69661.8	111664.3	256210.6	67947.4	1.2714	6.63645
Ethanol	20610.3	69418.6	107353.0	246701.7	65722.8	1.82189	6.61348
Ethanol	19852.0	69507.7	109703.5	251678.5	66843.7	1.05075	6.63151

Table S4. Training matrix for LDA of volatile organic compounds (Continued).

Sample	Intensity (peak area)					Canonical Score	
	421.7 nm	431.3 nm	512.9 nm	516.5 nm	563.4 nm	Factor (1)	Factor (2)
Ethanol	19803.8	66898.0	106957.7	245480.0	65216.0	0.28294	8.17213
Ethanol	19564.8	67485.3	108069.5	248135.4	65946.0	0.56064	7.78053
Acetic acid	14591.0	67740.6	22577.7	54256.5	15039.6	-35.38599	-28.69313
Acetic acid	14373.8	67137.1	23213.9	55740.6	15520.8	-35.23376	-27.86267
Acetic acid	14586.7	69347.3	24047.8	58002.2	16045.7	-34.39227	-29.98858
Acetic acid	14513.2	72398.8	23666.8	56866.5	15805.7	-35.20077	-32.97004
Acetic acid	14375.5	67524.8	22593.0	54642.8	14981.3	-35.25816	-29.20787
Acetic acid	15096.2	72851.9	22586.8	54077.5	14997.5	-35.47331	-33.2855
Acetic acid	14297.7	68755.2	22475.4	54260.2	15013.8	-35.54056	-30.2063
Acetic acid	14523.5	69329.7	23619.3	56820.6	15608.4	-35.03338	-30.30787
Acetic acid	14554.6	68821.2	23202.5	55525.7	15388.6	-35.49749	-29.44794
Acetic acid	14628.3	69564.3	24130.7	57550.3	15955.5	-35.22813	-29.6621
Butyl acetate	42254.6	157067.5	205265.9	476746.3	124587.9	65.18642	-35.5786
Butyl acetate	42071.5	161443.1	214421.5	496048.4	129855.3	65.89093	-35.32885
Butyl acetate	41651.4	157957.5	207145.1	480729.1	125807.8	64.80148	-35.72379
Butyl acetate	41728.2	160853.5	212296.3	491250.8	128897.9	65.08421	-35.20655
Butyl acetate	42188.1	160752.9	213054.6	492407.5	129293.9	65.18133	-33.88075
Butyl acetate	42294.9	161750.0	214058.7	493422.0	129543.3	63.74456	-33.62504
Butyl acetate	42472.9	159692.3	208368.0	482822.7	126705.2	65.40801	-35.17262
Butyl acetate	43678.0	165146.5	219952.9	507596.5	133455.8	68.53199	-33.83392
Butyl acetate	43616.6	160392.1	206231.0	476528.4	125016.6	63.85669	-34.86075
Butyl acetate	44096.5	163954.3	210609.8	485925.6	128022.8	65.39264	-34.94995
Ethyl acetate	20956.7	80907.8	115655.2	267839.9	71250.1	7.52748	-3.13327
Ethyl acetate	22039.9	82256.1	119341.0	275681.0	73601.2	9.52642	-1.27237
Ethyl acetate	22195.1	81254.4	118858.2	274827.8	73159.0	9.77824	-0.9252
Ethyl acetate	20695.6	81349.1	120423.2	277980.9	74395.7	8.31181	-0.56352
Ethyl acetate	21208.3	78269.2	114104.0	263808.4	70256.6	6.81767	-0.37632
Ethyl acetate	22207.5	82390.3	117541.9	271656.6	72482.6	9.11134	-2.11002
Ethyl acetate	20981.3	78358.2	116035.4	267637.1	71339.2	6.48848	0.59489
Ethyl acetate	21502.0	80643.6	119268.7	275502.0	73481.6	8.89856	-0.25669
Ethyl acetate	20522.3	81635.9	118498.2	272754.8	73391.7	6.49497	-0.39304
Ethyl acetate	20768.1	79989.9	119274.0	276090.6	73636.9	8.90359	-0.57764

Table S5. Testing matrix for LDA of volatile organic compounds.

Sample No.	Intensity					Allocated to group	Verification
	421.7 nm peak	431.3 nm peak	512.9 nm peak	516.5 nm peak	563.4 nm peak		
1	32739.4	96833.1	181784.8	408880.1	108309.4	Acetone	Yes
2	44321.7	171181.9	217372.0	501230.7	133428.9	Butyl acetate	Yes
3	2641.1	9333.4	1953.5	3476.7	920.3	Formic acid	Yes
4	14464.0	68405.3	23717.6	55590.6	15858.0	Acetic acid	Yes
5	19681.6	69949.4	112186.1	257545.1	68655.1	Ethanol	Yes
6	43909.9	168913.0	218974.7	503880.4	135225.0	Butyl acetate	Yes
7	32329.9	96376.8	177845.5	400063.8	106010.1	Acetone	Yes
8	43573.5	168488.6	217286.4	499370.0	133643.0	Butyl acetate	Yes
9	30781.3	95319.1	175666.9	395384.0	104863.8	Acetone	Yes
10	20574.8	77428.9	116312.8	267147.4	71536.1	Ethyl acetate	Yes
11	45219.1	171454.0	217300.6	501033.8	134493.4	Butyl acetate	Yes
12	31787.5	100279.4	204508.0	456576.9	123068.4	Butanone	Yes
13	20621.1	78751.3	117510.1	269717.8	72262.9	Ethyl acetate	Yes
14	2722.4	9498.9	2000.8	3474.5	962.5	Formic acid	Yes
15	19611.3	78619.9	115834.7	267329.5	71835.5	Ethyl acetate	Yes
16	19539.5	68894.0	109251.5	250375.9	66819.9	Ethanol	Yes
17	14627.8	70257.6	24239.8	56790.2	16479.1	Acetic acid	Yes
18	2347.1	8987.7	1790.4	2993.7	772.8	Formic acid	Yes
19	2559.9	9202.8	1873.1	3267.9	884.2	Formic acid	Yes
20	32074.6	94292.5	175374.3	394549.6	104558.5	Acetone	Yes
21	20563.1	77494.3	115629.5	265872.9	71155.8	Ethyl acetate	Yes
22	14980.8	68849.3	23512.9	55301.5	15851.2	Acetic acid	Yes
23	20047.8	78194.3	114885.1	265191.9	71271.5	Ethyl acetate	Yes
24	44933.0	173587.5	220854.1	508462.8	135117.6	Butyl acetate	Yes
25	31761.6	98485.7	184442.3	414181.4	109440.4	Acetone	Yes
26	8967.7	39350.2	13665.4	33543.1	9513.7	Methanol	Yes
27	21455.7	78360.4	117541.0	269597.2	72273.3	Ethyl acetate	Yes
28	44994.0	169884.4	215286.8	497521.2	131894.0	Butyl acetate	Yes
29	33060.1	106174.4	205948.7	459090.2	123939.2	Butanone	Yes
30	8869.5	39038.6	13454.2	33007.5	9436.0	Methanol	Yes
31	32121.7	91857.8	173401.2	390635.1	103166.2	Acetone	Yes
32	8709.0	37719.0	13021.5	31795.0	9106.1	Methanol	Yes
33	14485.4	68913.9	24221.9	56476.7	16343.1	Acetic acid	Yes
34	9085.5	40316.9	14301.9	34754.9	9913.4	Methanol	Yes
35	2549.7	9022.0	1865.7	3332.1	928.8	Formic acid	Yes
36	9040.7	39058.4	13346.7	32799.3	9378.4	Methanol	Yes
37	8814.4	38866.8	13624.7	33239.2	9506.1	Methanol	Yes
38	8821.0	37902.2	13108.0	31919.5	9122.2	Methanol	Yes
39	20013.6	68595.7	106503.7	244598.7	65257.8	Ethanol	Yes
40	30456.7	92364.2	172379.8	388752.6	103000.4	Acetone	Yes
41	21029.0	71430.1	110443.0	253444.5	67601.6	Ethanol	Yes
42	44955.0	169193.8	212198.5	491098.7	130686.6	Butyl acetate	Yes
43	2518.9	9326.7	1831.3	3235.5	873.1	Formic acid	Yes
44	14633.7	68889.8	23565.0	55990.2	15599.4	Acetic acid	Yes
45	2626.3	9455.4	1798.5	3266.0	857.4	Formic acid	Yes
46	2694.3	9505.7	1924.6	3461.8	968.5	Formic acid	Yes
47	31564.4	95705.2	181535.9	408484.1	108315.1	Acetone	Yes
48	2516.7	8983.7	1838.3	3327.4	926.5	Formic acid	Yes

Table S5. Testing matrix for LDA of volatile organic compounds (Continued).

Sample No.	Intensity					Allocated to group	Verification
	421.7 nm peak	431.3 nm peak	512.9 nm peak	516.5 nm peak	563.4 nm peak		
49	9180.8	39685.2	13815.1	33687.9	9706.5	Methanol	Yes
50	31857.2	100985.2	193672.6	433410.7	116824.7	Butanone	Yes
51	8859.7	38434.7	13133.4	32209.8	9221.5	Methanol	Yes
52	2717.4	9546.7	1936.6	3486.7	953.7	Formic acid	Yes
53	14504.3	67843.4	21971.0	51002.2	14777.0	Acetic acid	Yes
54	14922.8	68577.6	23127.7	54716.6	15384.2	Acetic acid	Yes
55	33151.5	105763.0	205098.7	457342.6	123218.9	Butanone	Yes
56	30093.5	91809.2	174176.0	392652.7	103699.4	Acetone	Yes
57	19782.8	69583.7	109914.8	251996.6	67276.3	Ethanol	Yes
58	32949.3	103744.9	210957.4	470108.5	126384.6	Butanone	Yes
59	33149.0	102897.2	202185.9	451644.5	121676.5	Butanone	Yes
60	20918.6	80025.4	118868.8	273725.3	73382.5	Ethyl acetate	Yes
61	20530.2	69443.6	108000.7	247701.0	66238.2	Ethanol	Yes
62	2552.6	9171.6	1846.1	3289.8	888.8	Formic acid	Yes
63	2717.5	9787.1	1913.7	3266.0	973.9	Formic acid	Yes
64	8969.9	38663.0	13097.6	32007.4	9165.0	Methanol	Yes
65	21246.3	80210.6	118423.9	272770.3	73051.8	Ethyl acetate	Yes
66	8726.8	37959.9	13057.7	32010.2	9118.9	Methanol	Yes
67	35080.9	102202.7	197169.2	441794.9	119303.1	Butanone	Yes
68	2457.2	9196.3	1757.2	3031.8	801.5	Formic acid	Yes
69	34219.9	102576.7	205861.2	461128.4	124397.3	Butanone	Yes
70	30822.5	93235.9	177050.5	399013.4	105469.4	Acetone	Yes
71	21567.2	82040.0	121479.7	279212.8	75123.1	Ethyl acetate	Yes
72	19808.9	68247.0	108335.6	248799.6	66368.7	Ethanol	Yes
73	8869.7	38469.1	13389.9	32530.0	9322.9	Methanol	Yes
74	43294.4	168462.4	218149.4	501605.5	133734.5	Butyl acetate	Yes
75	14290.7	67645.7	23633.6	54981.4	15835.8	Acetic acid	Yes
76	36197.1	105726.3	206212.3	460212.6	124154.7	Butanone	Yes
77	19925.8	69975.3	109947.2	252464.3	67199.8	Ethanol	Yes
78	20482.4	69731.4	108261.3	249003.2	66405.9	Ethanol	Yes
79	45259.4	170895.0	216529.0	498813.4	132838.5	Butyl acetate	Yes
80	14614.1	68494.0	23830.0	55992.1	15778.4	Acetic acid	Yes
81	14057.9	67286.1	23714.1	55353.0	15840.7	Acetic acid	Yes
82	44660.4	168243.6	212319.2	489610.3	130232.1	Butyl acetate	Yes
83	2634.5	9487.5	1906.6	3397.9	949.1	Formic acid	Yes
84	31614.3	102107.8	196924.8	439811.6	118672.5	Butanone	Yes
85	31453.7	100428.0	195700.0	437745.7	118062.6	Butanone	Yes
86	20681.9	78540.6	113842.7	263055.4	70309.7	Ethyl acetate	Yes
87	19694.4	68172.1	107666.6	247195.4	65772.8	Ethanol	Yes
88	44740.0	170609.2	222696.1	512290.3	137727.4	Butyl acetate	Yes
89	30794.1	96018.3	188953.5	422114.6	112939.4	Acetone	No
90	19515.0	69142.2	109852.2	252015.0	67075.1	Ethanol	Yes
91	31889.0	95920.6	178599.5	402490.6	106332.9	Acetone	Yes
92	8909.8	37822.5	13154.1	31703.6	9129.4	Methanol	Yes
93	30561.4	95858.5	177134.8	398850.1	105793.8	Acetone	Yes
94	44811.8	171364.8	218990.5	506191.8	134346.8	Butyl acetate	Yes
95	20294.3	68773.1	106235.2	244801.8	65168.4	Ethanol	Yes
96	8996.0	39168.9	13838.7	33767.5	9700.0	Methanol	Yes
97	2529.7	9184.6	1808.2	3223.4	857.8	Formic acid	Yes

Table S5. Testing matrix for LDA of volatile organic compounds (Continued).

Sample No.	Intensity					Allocated to group	Verification
	421.7 nm peak	431.3 nm peak	512.9 nm peak	516.5 nm peak	563.4 nm peak		
98	2554.4	9113.3	1797.2	3212.7	849.1	Formic acid	Yes
99	44635.4	163159.6	206905.8	478178.9	125991.4	Butyl acetate	Yes
100	43677.6	166257.8	215260.7	496722.5	131271.1	Butyl acetate	Yes
101	8856.7	37716.5	13158.6	31983.6	9243.0	Methanol	Yes
102	20623.4	70526.0	109617.5	251997.0	67396.5	Ethanol	Yes
103	33656.1	106566.7	205393.2	458584.1	123888.8	Butanone	Yes
104	32682.1	102431.1	201361.8	450308.9	121443.4	Butanone	Yes
105	29993.9	91177.8	178300.9	402003.9	106212.8	Acetone	Yes
106	21190.0	75854.1	109676.2	252594.6	67701.3	Ethyl acetate	Yes
107	30923.2	92159.0	180181.3	406036.0	107233.1	Acetone	Yes
108	14543.7	68949.5	24028.4	56370.7	16207.2	Acetic acid	Yes
109	21286.1	79879.5	116321.6	267853.8	71867.8	Ethyl acetate	Yes
110	20820.3	69905.9	107356.5	246299.8	65793.5	Ethanol	Yes
111	14732.4	70421.4	24742.8	58535.4	16506.6	Acetic acid	Yes
112	44748.7	172268.9	225355.5	517488.3	138778.1	Butyl acetate	Yes
113	31315.3	93652.0	178203.5	400852.9	105757.5	Acetone	Yes
114	14261.3	68910.8	23989.0	55442.6	16488.5	Acetic acid	Yes
115	2520.1	9211.2	1832.4	3245.0	914.4	Formic acid	Yes
116	44837.6	170112.7	215610.2	497701.4	132529.8	Butyl acetate	Yes
117	15007.0	68190.5	23450.1	55068.7	15697.4	Acetic acid	Yes
118	15552.5	75088.1	25242.2	59605.1	17000.4	Acetic acid	Yes
119	21212.2	79510.0	114111.0	262981.5	70595.7	Ethyl acetate	Yes
120	19518.1	68562.9	108914.0	250109.3	66503.1	Ethanol	Yes
121	30401.5	92310.2	171422.3	384841.7	101941.5	Acetone	Yes
122	14482.2	69202.1	24429.0	57243.5	16332.0	Acetic acid	Yes
123	31722.9	95012.3	178957.5	403049.0	106514.8	Acetone	Yes
124	33040.0	103889.0	208066.4	464347.5	125329.1	Butanone	Yes
125	14820.5	69067.4	23228.2	54633.1	15515.0	Acetic acid	Yes
126	32188.1	101389.7	203963.7	455710.5	122889.3	Butanone	Yes
127	31842.5	100527.3	196642.8	440461.0	118584.0	Butanone	Yes
128	19495.1	68300.4	108785.9	249480.3	66539.7	Ethanol	Yes
129	20866.7	79207.4	118758.9	273414.6	73221.4	Ethyl acetate	Yes
130	2484.7	8906.7	1840.4	3260.7	935.2	Formic acid	Yes
131	20103.6	78213.7	115496.0	265752.4	71279.2	Ethyl acetate	Yes
132	45305.3	165683.5	206798.7	479080.5	126707.2	Butyl acetate	Yes
133	32418.7	100996.5	194832.8	436132.4	117702.3	Butanone	Yes
134	21102.4	79128.4	115083.5	265311.0	70848.3	Ethyl acetate	Yes
135	32331.0	101424.4	195279.9	436831.5	117777.2	Butanone	Yes
136	20694.2	78921.7	117813.8	271838.1	72637.7	Ethyl acetate	Yes
137	31943.3	94872.4	176765.4	398074.4	105672.8	Acetone	Yes
138	20364.0	79802.5	117993.6	271267.4	72951.9	Ethyl acetate	Yes
139	21961.4	77881.6	112359.5	258613.4	69238.9	Ethyl acetate	Yes
140	8751.6	37981.1	13178.3	32042.7	9218.9	Methanol	Yes
141	45198.9	169767.0	216938.2	501289.0	132637.0	Butyl acetate	Yes
142	9100.7	39917.2	14161.1	34563.6	9923.9	Methanol	Yes
143	19891.5	68871.0	107980.9	248418.1	66347.8	Ethanol	Yes
144	44638.9	166188.9	206629.7	478300.1	126957.0	Butyl acetate	Yes
145	14914.2	67557.0	23424.6	54712.8	15684.0	Acetic acid	Yes
146	14737.5	68228.6	23576.2	55446.3	15896.7	Acetic acid	Yes

Table S5. Testing matrix for LDA of volatile organic compounds (Continued).

Sample No.	Intensity					Allocated to group	Verification
	421.7 nm peak	431.3 nm peak	512.9 nm peak	516.5 nm peak	563.4 nm peak		
147	14133.9	68416.6	23667.6	54969.1	15829.5	Acetic acid	Yes
148	8747.4	37888.6	12840.5	31576.1	9116.8	Methanol	Yes
149	19557.3	68500.8	107993.0	247860.5	66070.5	Ethanol	Yes
150	8813.4	38141.3	13019.0	31845.5	9095.8	Methanol	Yes
151	2802.6	9693.7	1863.1	3360.4	911.4	Formic acid	Yes
152	32137.4	98884.0	190836.8	426300.3	114191.6	Acetone	No
153	9272.9	38953.9	13305.2	32229.0	9289.4	Methanol	Yes
154	32025.1	97529.1	180433.0	406353.0	107831.2	Acetone	Yes
155	31562.0	95357.9	177248.3	399008.8	105761.3	Acetone	Yes
156	19266.8	68884.4	110106.2	252701.1	67240.0	Ethanol	Yes
157	21243.9	81290.8	118591.8	272259.3	73134.6	Ethyl acetate	Yes
158	47354.6	173392.1	209649.5	484302.2	128615.2	Butyl acetate	Yes
159	2289.7	8980.2	1763.5	3143.0	794.1	Formic acid	Yes
160	19744.4	70337.1	112721.8	258379.6	68957.3	Ethanol	Yes

Table S6. Classification data for LDA of wines.

Wine NO.	Intensity (peak area)					Canonical Score	
	421.7 nm	431.3 nm	512.9 nm	516.5 nm	563.4 nm	Factor (1)	Factor (2)
1	12617.8	63034.4	47344.0	121303.4	2737.8	17.55784	-8.14647
1	12042.9	61674.4	46805.0	118605.2	2671.0	16.69717	-9.59002
1	13943.4	63954.0	51117.7	127953.2	2763.5	19.5893	-9.69575
1	14203.5	65933.4	53048.3	133299.8	2866.0	21.86869	-10.19862
1	13783.5	65520.2	52235.1	130954.5	2849.6	21.18091	-10.69345
1	14509.4	66931.3	52675.9	131997.6	2836.8	21.70425	-10.28289
1	14351.1	67393.0	53194.3	133624.4	2931.5	22.25755	-10.36285
1	14496.5	67241.7	52781.5	132579.1	2937.7	21.66296	-9.79856
1	14173.5	66066.6	51795.4	129516.4	2886.7	20.45382	-10.04435
1	13811.2	64847.1	50894.0	127193.8	2845.3	19.47158	-9.97947
2	9786.2	50669.7	38332.9	96000.6	1753.8	8.59936	-10.09032
2	10181.8	52154.7	38387.2	96132.9	1850.5	8.62176	-9.58051
2	10510.8	52008.1	37378.4	94242.4	1926.7	7.26517	-7.60657
2	11404.7	53818.4	38379.9	96804.7	2049.6	7.8898	-6.60469
2	11204.7	53226.1	37280.3	92305.4	1813.6	7.06513	-8.49784
2	11349.6	54417.8	38215.9	96741.5	1978.0	8.41683	-7.00383
2	11698.4	56019.5	38468.2	97233.9	2126.0	8.47188	-6.5779
2	11886.4	57742.7	38902.1	98960.1	2070.9	9.90609	-7.03955
2	12362.5	58698.0	38770.5	98732.5	2136.3	9.62055	-6.128
2	12147.5	58634.5	38663.4	98934.3	2180.1	9.63299	-5.92074
3	17234.2	68362.8	37877.2	103857.1	2782.4	9.24186	7.22039
3	15741.0	65981.7	37286.3	101544.1	2889.1	8.06852	5.71951
3	15623.8	67289.2	38210.8	104056.4	3020.7	9.15693	5.22591
3	15767.6	67187.8	38469.7	105326.1	3039.9	9.38613	5.93104
3	15796.3	68125.7	36954.0	103289.0	2974.2	9.13744	7.18518
3	14397.7	67899.7	38006.2	108723.7	3298.4	10.74138	7.60877
3	15033.6	69319.8	37893.0	107742.8	3297.3	10.54941	7.73903
3	15416.4	70162.0	38059.7	108094.1	3276.0	10.84866	7.85088
3	15229.8	69640.9	37471.9	106648.8	3332.4	9.99083	8.30963
3	15017.1	69729.3	37933.9	106992.9	3336.2	10.34685	7.11016
4	14521.5	64799.0	38159.8	100809.6	2738.1	8.91983	0.82186
4	14668.1	66484.6	38932.9	103794.3	2833.1	10.25027	1.13202
4	14338.3	65397.3	38132.8	101878.6	2794.4	9.43763	1.26627
4	14910.0	68110.1	39164.3	104567.3	2922.2	10.70868	1.30152
4	14738.6	66145.6	37790.5	101561.0	2806.8	9.26418	2.27496
4	15347.3	68746.0	39037.5	105235.7	2933.2	10.81825	2.62278
4	15173.2	67825.2	37858.2	101830.7	2875.0	9.49744	2.69814
4	15316.3	69504.9	39392.0	106155.0	2979.0	11.33872	2.29152
4	14991.7	68971.7	38661.8	104101.1	2960.5	10.64527	2.03586
4	15317.2	69784.5	38998.5	105224.8	2966.2	11.14677	2.3355
5	4299.4	15803.3	8864.5	17740.7	707.7	-27.96978	1.60022
5	4757.0	16721.1	8719.8	17353.3	732.6	-28.15577	2.2194
5	4537.3	15838.8	8483.5	16557.6	792.3	-28.89427	2.46614
5	4690.6	16585.3	8676.9	17137.4	873.6	-28.7843	2.77897
5	4975.3	16810.5	8838.3	17799.9	933.1	-28.88564	3.59434
5	4194.1	14508.8	8592.0	16658.9	905.3	-29.59658	2.79287
5	4861.4	16365.8	8709.4	17428.2	870.1	-28.88948	3.30827
5	4216.5	15543.1	9238.8	19132.0	1093.9	-28.99769	3.53947
5	4257.7	15772.5	8841.8	17012.4	1054.9	-29.52897	2.75361

Table S6. Classification data for LDA of wines (Continued).

Wine NO.	Intensity (peak area)					Canonical Score	
	421.7 nm	431.3 nm	512.9 nm	516.5 nm	563.4 nm	Factor (1)	Factor (2)
5	3930.9	14494.6	8656.6	16681.7	1033.8	-29.88776	2.79453
6	18312.4	75685.4	42172.0	116873.7	4151.3	11.16993	11.96088
6	18240.5	78905.1	44772.4	125091.1	4490.6	14.34265	11.89853
6	18583.3	76506.7	43345.7	121715.3	4381.3	12.18567	13.92636
6	19696.0	80385.9	44513.1	124359.2	4485.1	13.65525	14.0092
6	19012.5	79419.9	44009.9	123091.4	4517.4	13.13337	13.55522
6	18738.3	79642.6	43963.1	122569.5	4514.8	13.26131	12.67524
6	19219.6	78476.3	43454.9	121345.5	4477.3	12.0852	14.204
6	19277.6	79561.5	44389.9	125021.9	4730.0	12.86687	15.48996
6	19878.7	81657.0	44709.0	125509.4	4932.1	12.7474	16.27741
6	19315.5	80676.7	44041.8	123691.5	4929.4	12.063	15.87331
7	3288.9	11709.6	7116.9	10905.7	424.8	-30.36827	-0.63529
7	3084.5	11831.1	7348.0	11062.8	443.3	-30.15445	-1.38461
7	2633.0	10829.3	6944.3	10014.0	432.2	-30.60857	-1.66396
7	2907.1	11669.8	6956.9	9895.8	401.0	-30.36771	-1.78463
7	2749.6	11417.0	6622.4	9487.1	438.0	-30.6833	-1.33433
7	2378.7	11275.2	6213.3	8169.2	409.1	-30.8503	-2.10576
7	2039.1	11571.7	6682.7	8963.9	464.5	-30.36254	-3.0997
7	2322.8	12061.9	6738.3	9387.5	478.5	-30.26883	-2.55328
7	1880.7	11786.6	6458.9	8573.9	460.5	-30.29914	-3.2874
7	1538.2	11441.3	6399.7	8232.9	444.8	-30.25549	-3.95282
8	10595.9	47800.8	30141.4	71899.5	1568.5	-1.53825	-6.61703
8	10826.6	49483.5	30100.1	72241.1	1678.3	-1.30671	-6.0905
8	10558.4	48021.3	28928.6	68799.2	1541.0	-2.49602	-6.36989
8	10393.7	46956.7	28236.0	66752.9	1577.1	-3.73516	-5.90177
8	10600.2	48331.4	29272.0	70244.0	1593.9	-2.07724	-5.94625
8	9764.6	46280.6	28673.3	68281.6	1601.1	-3.09409	-6.58201
8	11364.5	49951.9	30415.2	72433.9	1647.2	-1.27302	-5.99995
8	10947.6	49225.6	29948.8	71148.9	1701.6	-1.97307	-6.04759
8	11437.8	50795.2	30186.9	72296.1	1747.9	-1.43204	-5.35184
8	11070.1	49556.8	29522.0	70142.4	1674.1	-2.20488	-5.84787

Table S7. Classification data for LDA of four isomers.

Sample	Intensity (peak area)					Canonical Score	
	421.7 nm	431.3 nm	512.9 nm	516.5 nm	563.4 nm	Factor (1)	Factor (2)
Ether	8319.1	39801.5	42839.5	132549.2	33031.5	16.00379	-2.11154
Ether	8335.2	35826.0	40954.6	123669.4	30796.0	18.34936	-3.02678
Ether	8695.8	41056.5	43562.3	135208.4	33758.0	16.14306	-1.98296
Ether	7173.8	32601.8	37247.6	113955.5	28344.2	18.36926	-3.9226
Ether	7972.8	37629.2	41065.7	126712.7	31551.8	16.55493	-2.84505
Ether	8073.0	38657.8	44300.3	137200.6	34106.0	15.81576	-0.88015
Ether	8394.1	38699.0	42136.7	131410.8	32809.9	16.82044	-2.48472
Ether	9117.1	40434.5	46468.5	143401.7	35758.2	16.75672	-0.51531
Ether	8022.5	35999.0	38978.5	120517.2	30157.1	18.79738	-3.29636
Ether	8081.1	36321.4	40660.2	126374.0	31593.4	18.47118	-2.29429
Isobutanol	12693.1	68893.4	70149.8	218167.1	53854.3	-0.85832	3.68793
Isobutanol	12709.9	67919.5	69851.9	217463.0	53714.9	-0.03242	3.78005
Isobutanol	13047.4	69858.7	72203.2	224530.3	55530.1	0.29262	5.55853
Isobutanol	13788.3	73812.6	74629.7	231205.2	57097.7	-2.37094	4.70456
Isobutanol	13693.3	72247.4	73230.0	226527.6	56155.9	1.33638	6.2403
Isobutanol	13501.9	71788.9	72739.9	225451.5	55890.0	1.37963	6.24067
Isobutanol	13510.0	71534.1	73365.6	227648.2	56316.1	-0.12151	5.48511
Isobutanol	14226.5	75275.3	76701.9	237202.5	58648.6	-1.80446	6.0715
Isobutanol	14428.8	77040.6	77822.4	239374.7	59281.2	-0.7238	7.73078
Isobutanol	14189.2	75396.9	75581.6	233206.3	57703.8	-1.22517	5.76975
1-Butanol	13092.2	72731.6	70705.1	220627.7	53875.7	-11.29697	-3.69521
1-Butanol	12797.8	71783.8	71679.6	224994.3	54854.2	-12.4972	-3.39684
1-Butanol	12223.6	69056.3	69198.7	216996.0	52860.8	-11.42218	-3.88109
1-Butanol	13316.8	73137.1	70844.2	221280.4	54020.4	-11.8833	-4.45108
1-Butanol	12645.2	68918.6	68922.6	216505.5	52784.1	-11.08941	-4.87248
1-Butanol	12591.5	69659.2	68159.1	213920.5	52100.2	-12.10157	-5.89251
1-Butanol	12417.1	69247.1	69382.4	218741.0	53380.4	-10.81248	-3.64641
1-Butanol	13046.2	71812.6	71377.9	223546.7	54542.7	-11.80417	-3.69827
1-Butanol	13881.6	77577.5	73620.4	229826.9	56202.5	-12.875	-3.17666
1-Butanol	13572.3	75026.2	71887.5	224689.5	54989.6	-11.06734	-3.09807
2-Butanol	13063.3	71676.3	71031.9	220302.7	54205.4	-4.46158	1.49997
2-Butanol	13231.3	72302.4	71114.6	220809.6	54279.8	-5.63503	0.45198
2-Butanol	13265.3	70779.5	69836.4	216437.8	53228.2	-4.52579	-0.20321
2-Butanol	13261.1	72551.6	71276.7	221142.8	54390.6	-5.28099	0.84063
2-Butanol	13400.7	72242.3	71602.3	222754.6	54704.8	-6.53892	-0.27612
2-Butanol	13127.0	71535.4	71796.2	223067.3	54949.5	-3.60576	2.55475
2-Butanol	13051.3	71608.3	70686.8	219989.9	54131.8	-4.73517	1.06148
2-Butanol	12902.9	71327.2	70426.0	219237.5	53919.7	-4.96698	0.96198
2-Butanol	13072.0	71295.5	71060.9	221855.6	54527.8	-5.71715	0.47887
2-Butanol	13283.2	71602.0	71600.1	223388.2	54918.8	-5.63689	0.52886

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