Supplementary Materials

Determination of Volatile Fuel Oxygenates in Water by Gas Chromatography–Triple Quadrupole Mass Spectrometry: Effect of Automated Sample Preparation Techniques

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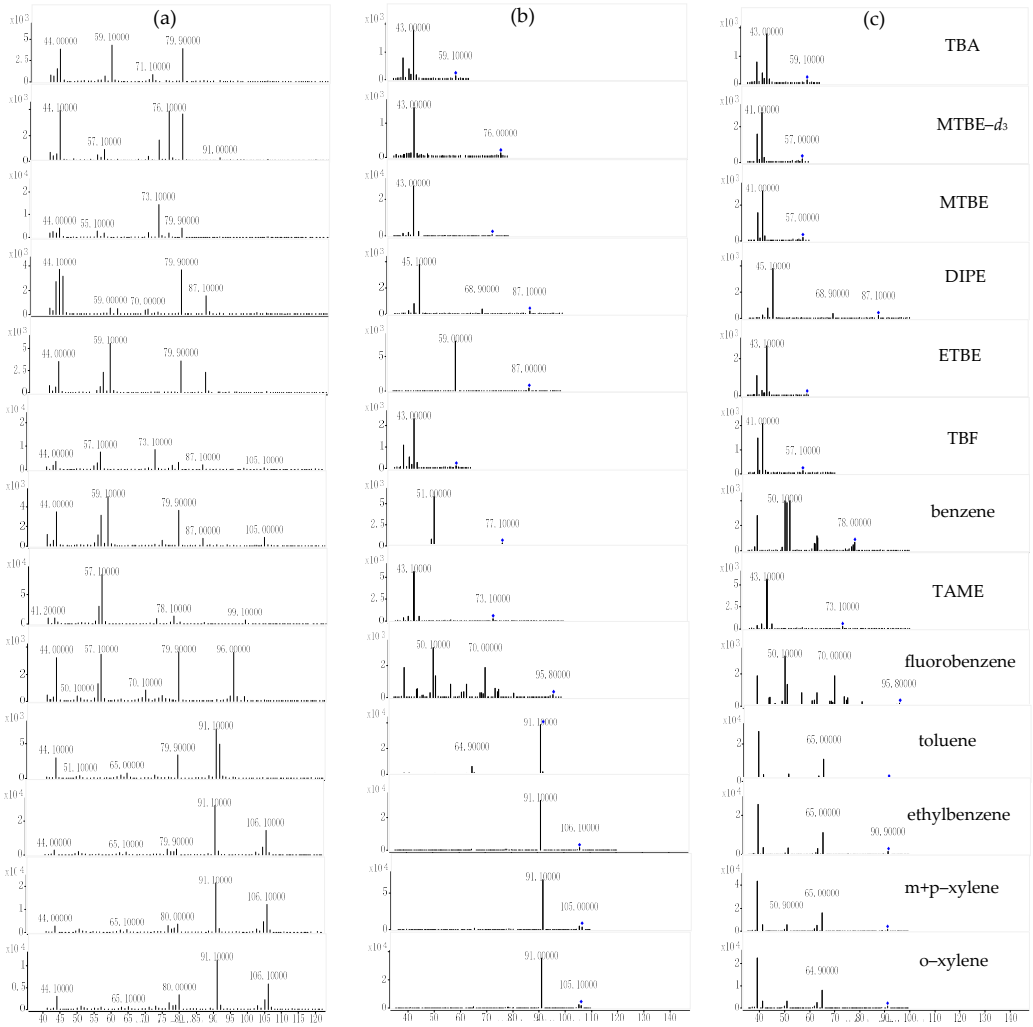

Figure 1. The mass spectra of the twelve analytes: (a) Full scan spectra in EI mode; (b) Daughter scan spectra of quantitative ions; (c) Daughter scan spectra of qualitative ions.

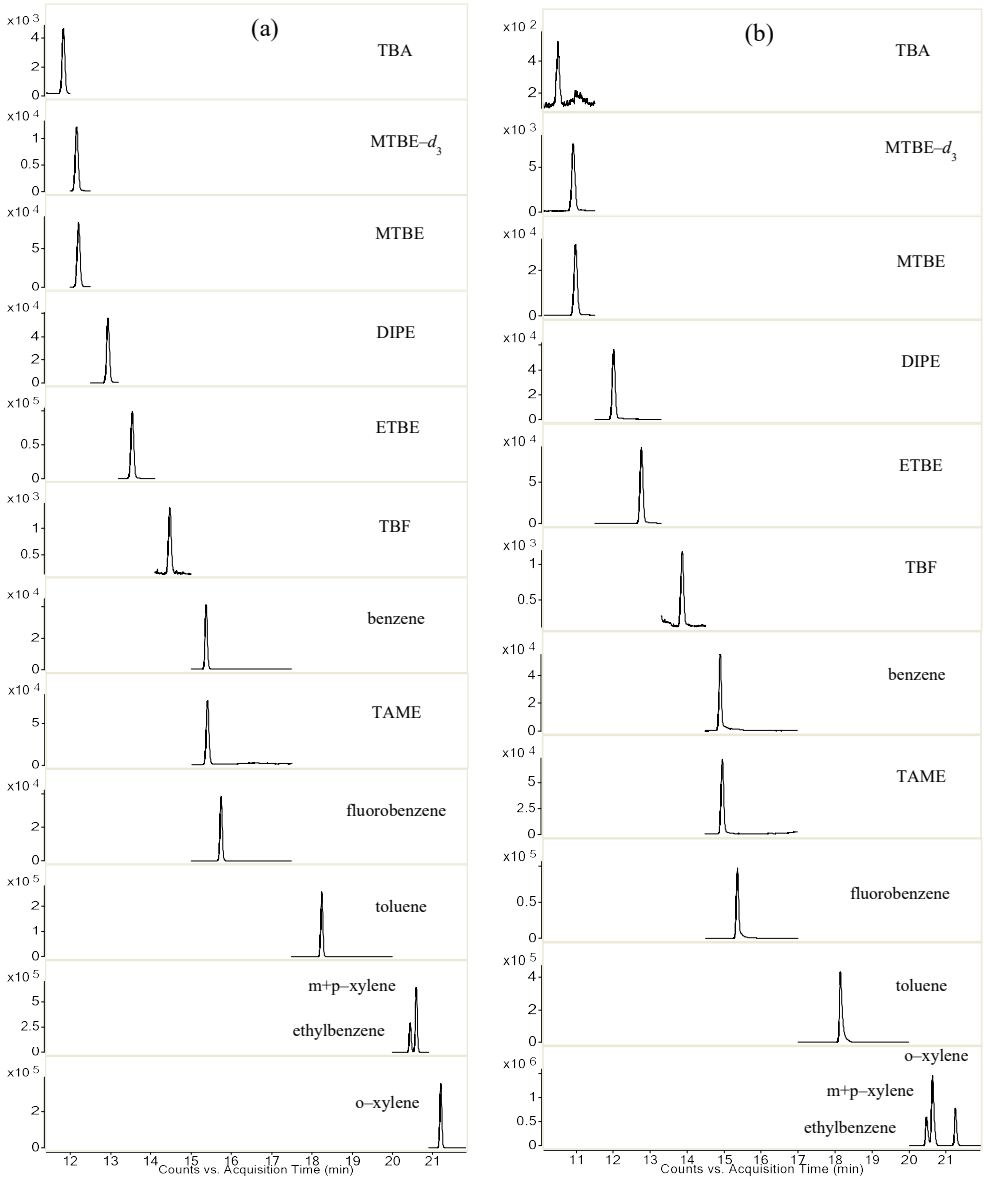

Figure S2. Chromatograms of quantitative identification ions of the twelve analytes (5 μg/L) in MRM: (a) PT–GC–MS/MS chromatograms; (b) HS–SPME–GC–MS/MS chromatograms.

Table S1. Name, segments, retention time, dwell time, precursors and product ions of quantitative transition and confirmation transition, and collision energy for the twelve analytes.

Analyte	segment	RT[1] (min)	DT[2] (ms)	Quantitative transition (Q)			Confirmation transition (q)		
				Precursor ion (*m/z*)	Product ion (*m/z*)	CE[3]	Precursor ion (*m/z*)	Product ion (*m/z*)	CE[3]
TBA	**1**	**12.2**	240	59.1$[CH_3COHCH_3]^+$	43.0$[CH_3CHCH_3]^+$	22	59.1$[CH_3COHCH_3]^+$	39.1$[CHCHCH]^+$	22
IS_1	2	12.5	120	76.1$[C_3H_6D_3CO]^+$	43.0$[CH_3CO]^+$	22	57.1$[C_2H_5CO]]^+$	41.0$[C_2H_5C]^+$	11
MTBE	2	12.6	120	73.1$[C_3H_9CO]^+$	43.0$[CH_3CO]^+$	22	57.0$[C_2H_5CO]^+$	41.0$[C_2H_5C]^+$	11
DIPE	3	13.3	120	87.1$[C_2H_6CHOHCHCH_3]^+$	45.1$[CH_3CH_2O]^+$	4	87.1$[C_2H_6CHOHCHCH_3]^+$	43.1$[CH_3CO]^+$	4
ETBE	3	13.9	120	87.0$[C_3H_9COCH_2]^+$	59.0$[C_2H_5OCH_2]^+$	8	59.1$[C_2H_5OCH_2]^+$	43.1$[C_2H_3O]$	24
TBF	4	14.8	240	59.1$[C_2H_6CHO]^+$	43.0$[C_2H_6CH]^+$	22	57.1$[COCHO]^+$	41.0$[COCH]^+$	13
Benzene	5	15.7	80	77.1$[C_6H_5]^+$	51.0$[C_4H_3]^+$	20	78.0$[C_6H_6]^+$	52.1$[C_4H_4]^+$	28
TAME	5	15.7	80	73.1$[C_2H_6COCH_2]^+$	43.1$[CH_2OCH]^+$	22	73.1$[C_2H_6COCH_2]^+$	45.1$[CH_2OCH_3]^+$	22
IS_2	5	16.1	80	96.0$[C_6H_5F]^+$	70.0$[C_3H_2CH_2F]^+$	35	96.0$[C_6H_5F]^+$	50.1$[C_4H_2]^+$	35
Toluene	6	18.6	240	92.1$[C_7H_8]^+$	64.9$[C_5H_5]^+$	18	92.1$[C_7H_8]^+$	39.1$[C_3H_3]^+$	29
Ethylbenzene	7	20.8	80	106.1$[C_8H_{10}]^+$	91.1$[C_7H_8]^+$	13	91.1$[C_7H_8]^+$	39.1$[C_3H_3]^+$	31
m+p–xylene	7	20.9	80	106.1$[C_8H_{10}]^+$	91.1$[C_7H_8]^+$	13	91.1$[C_7H_8]^+$	39.1$[C_3H_3]^+$	31
o–xylene	7	21.5	80	106.1$[C_8H_{10}]^+$	91.0$[C_7H_8]^+$	13	91.1$[C_7H_8]^+$	39.1$[C_3H_3]^+$	31

[1]RT: retention time; [2]DT: dwell time; [3]CE: collision energy; IS_1: MTBE–d_3; IS_2: Fluorobenzene.

Table S2. Linearity of standard calibration curves, LODs, LOQs, method precision and validity for the twelve analytes using the P&T–GC–QqQ–MS/MS methodology.

Analyte	Linear range (μg/L)	r^2	LODs (ng/L)	LOQs (ng/L)	RSD%				Recovery (%)			
					Intra–day (n=5)		Inter–day (n=6)		Surface water		Groundwater	
					0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L
TBA	0.10~20	0.9998	32.00	96.00	8.19	6.95	5.43	9.33	109.3 ± 3.9	111.2 ± 1.7	120.1 ± 6.7	114.2 ± 6.7
MTBE	0.05~20	0.9997	0.70	2.10	2.39	5.50	2.28	3.09	103.8 ± 4.1	90.9 ± 3.0	91.1 ± 3.7	90.4 ± 5.4
DIPE	0.05~20	0.9992	0.67	2.01	3.11	4.40	2.89	7.94	96.3 ± 5.2	104.9 ± 5.0	85.5 ± 2.9	104.9 ± 2.0
ETBE	0.05~20	0.9998	0.62	1.86	3.05	5.95	1.99	6.81	114.2 ± 0.5	83.1 ± 2.6	81.6 ± 1.7	84.1 ± 3.1
TBF	0.20~20	0.9965	0.62	1.86	3.18	8.87	3.30	12.7	98.8 ± 4.8	80.2 ± 2.1	96.8 ± 1.8	84.3 ± 3.6
Benzene	0.05~20	0.9992	0.55	1.65	2.38	4.62	2.37	6.09	91.0 ± 0.4	82.6 ± 0.7	83.5 ± 5.9	81.1 ± 1.3
TAME	0.05~20	0.9996	12.70	38.10	6.14	6.50	1.18	4.27	102.7 ± 3.6	90.9 ± 2.3	97.0 ± 1.8	92.3 ± 1.4
Toluene	0.05~20	0.9994	0.55	1.65	3.37	8.16	3.03	5.31	88.9 ± 2.0	103.6 ± 3.8	89.1 ± 1.8	109.6 ± 2.0
Ethylbenzene	0.05~20	0.9992	0.53	1.59	2.38	6.43	1.28	7.93	108.1 ± 1.9	80.8 ± 2.4	109.3 ± 1.2	80.5 ± 1.3
m+p–xylene	0.05~20	0.9993	0.52	1.56	1.99	6.09	3.49	5.61	107.2 ±1.8	83.5 ± 4.4	106.1 ± 8.3	80.7 ± 4.3
o–xylene	0.05~20	0.9993	0.59	1.77	2.16	2.83	5.18	7.98	111.4 ± 1.9	85.0 ± 3.7	105.9 ± 6.5	86.2 ± 3.1

Table S3 Linearity of standard calibration curves, LODs, LOQs, method precision and validity for the twelve analytes using the HS–SPME–GC–MS/MS methodology.

Analyte	Linear range (μg/L)	r^2	LODs (ng/L)	LOQs (ng/L)	RSD%				Recovery (%)			
					Intra–day (n=5)		Inter–day (n=6)		Surface water		Groundwater	
					0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L	0.5 μg/L	5 μg/L
TBA	0.50~20	0.9961	151.00	453.00	2.03	7.09	6.70	7.88	107.7 ± 8.5	115.4 ± 3.9	83.0 ± 3.9	114.4 ± 1.1
MTBE	0.05~20	0.9976	1.43	4.29	6.19	9.65	5.46	7.46	96.7 ± 3.9	117.4 ± 5.5	87.5 ± 4.5	95.6 ± 0.5
DIPE	0.05~20	0.9992	1.40	4.20	2.71	1.44	6.32	8.46	95.9 ± 2.3	102.2 ± 7.3	82.6 ± 2.9	73.0 ± 1.4
ETBE	0.05~20	0.9993	0.92	2.76	1.81	5.57	1.59	1.09	97.0 ± 1.4	103.3 ±10.7	84.0 ± 4.8	80.5 ± 5.7
TBF	0.20~20	0.9996	44.00	132.00	3.19	5.35	1.17	7.72	73.9 ± 8.3	109.3 ± 5.0	75.2 ± 1.8	91.8 ± 3.9
Benzene	0.05~20	0.9974	0.11	0.33	2.45	8.48	5.13	7.55	85.4 ± 7.1	104.9 ± 9.4	73.8 ± 3.7	73.7 ± 4.1
TAME	0.10~20	0.9999	28.70	86.10	1.49	9.36	4.12	4.12	116.2 ± 2.3	123.1 ± 7.6	106.4 ± 1.6	79.3 ± 7.4
Toluene	0.05~20	0.9975	0.34	1.02	1.64	7.73	2.38	7.71	99.8 ± 8.0	84.0 ± 2.0	105.0 ± 8.2	82.2 ± 7.6
Ethylbenzene	0.05~20	0.9964	0.33	0.99	2.18	6.47	4.09	5.11	123.8 ± 8.5	92.4 ± 6.9	117.4 ± 6.2	77.7 ± 5.8
m+p–xylene	0.05~20	0.9967	0.38	1.14	1.19	5.63	1.36	8.14	120.1 ± 9.6	94.7 ± 3.6	113.6 ± 6.3	75.3 ± 8.3
o–xylene	0.05~20	0.9978	0.27	0.81	2.05	7.35	3.02	9.78	111.4 ± 9.6	101.7 ± 4.1	103.1 ± 6.6	93.9 ± 7.2