Electronic   Supplementary   Information

High temperatures to obtain ion mobilities decreasing uncertainties caused by clustering

Roberto Fernández-Maestre,[1] Martha C. Daza[2]

Fig. S1 Photograph of the IMS-MS instrument
Fig. S2 Structures of compounds
Fig. S3 K_0 behavior of phenylalanine and tryptophan with buffer gas temperature and contaminant concentration
Fig. S4-S6 Additional spectra
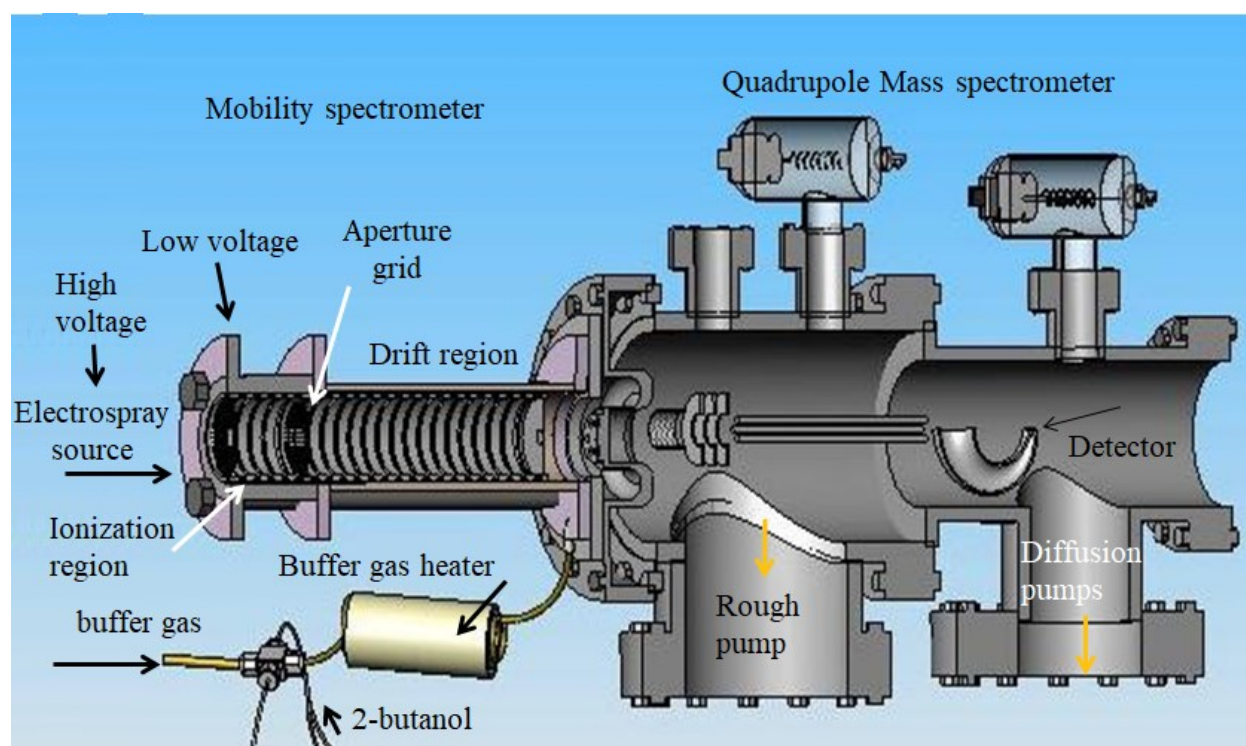Tables S1-S6 Complete data tables

Fig. S1 Cross section of the IMS-MS instrument

[1] Departamento de Quimica, Campus de San Pablo, Universidad de Cartagena, Cartagena, Colombia. rfernandezm@unicartagena.edu.co

Moscow Engineering Physics Institute. National Research Nuclear University. Russia Orcid ID 0000-0001-6791-5318

[2] Grupo de Bioquímica Teórica, Universidad Industrial de Santander, Cra 27 Calle 9, Bucaramanga, Colombia.
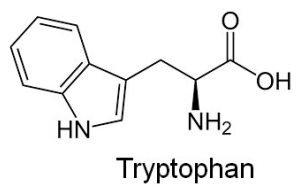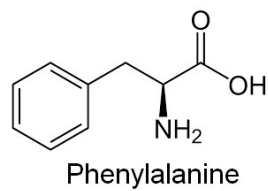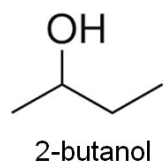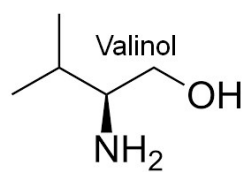
Fig. S2 Structures of compounds used in this study
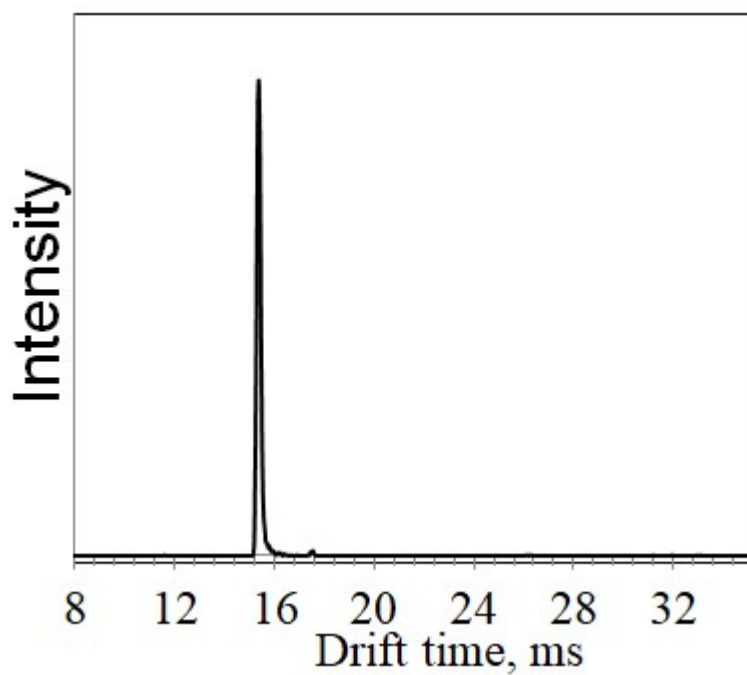
Fig. S3 SIM spectrum of the ESI solution when 6.8 mmol m^{-3} of 2-butanol were injected in the buffer gas at 100 °C. The spectrum was obtained at m/z 54-56.
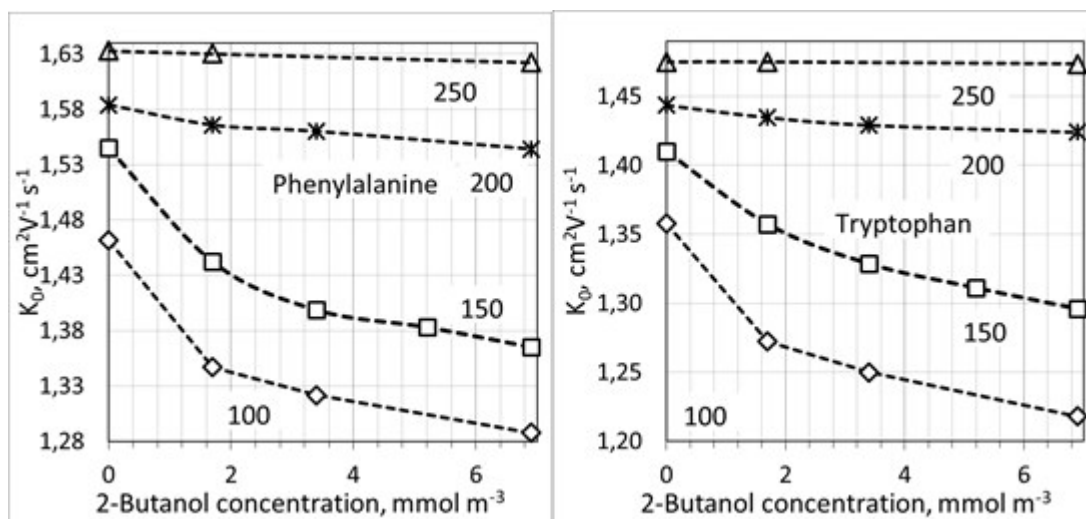
Fig. S4 K_0 behavior of phenylalanine and tryptophan (100-µM solution) with the increase in buffer gas temperature and contaminant concentration. Changes in reduced mobilities as buffer gas temperature increased were produced by a reduction in clustering with 2-butanol and, as concentration of 2-butanol increased, by an increased clustering. Other experimental conditions were kept constant. K_0s were obtained with Equation 3; DTBP was the chemical standard in similar experimental conditions, K_0 1.42 cm^{2}V^{-1}s^{-1}.[7]
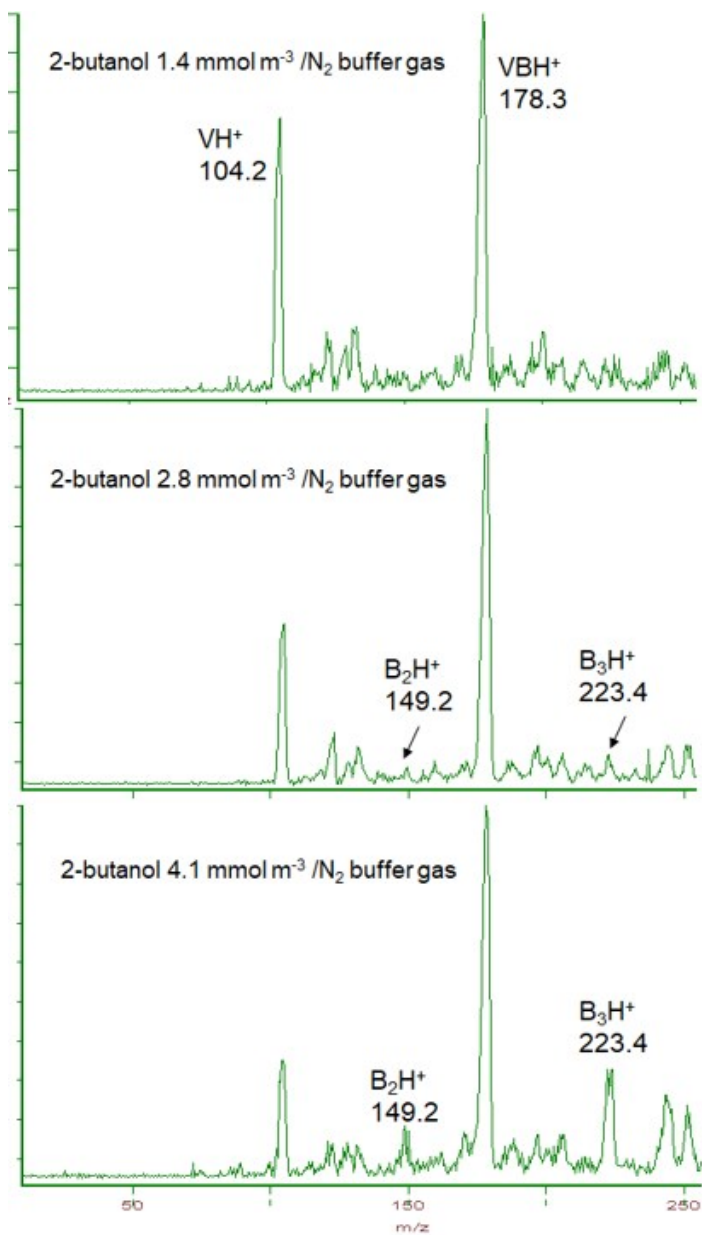
Fig. S5 Effect of 2-butanol concentration in the buffer gas on the abundance of clusters in the mass spectra of valinol at 150°C. Other experimental conditions were kept constant. As the 2-butanol concentration increases, the ratio VBH^+ / VH^+ increases due to extensive clustering. Other cluster peaks such as VH_3O, B_3H^+ and VBH_3O^+ also increase for the same reason.
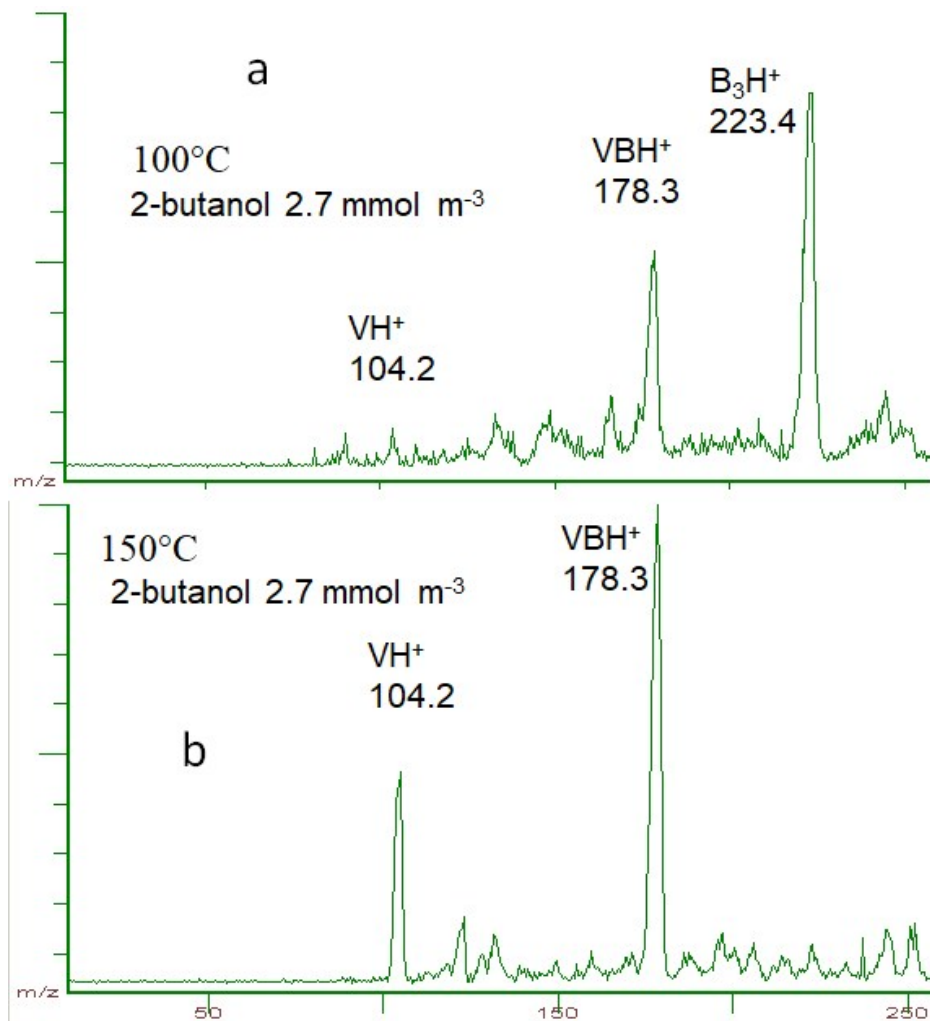
Fig. S6 Mass spectra of valinol at 100°C and 150°C at the same 2-butanol concentration, 2.7 mmol m^{-3}. Other experimental conditions were kept constant. At 100°C, the protonated valinol peak is very small and the ratio VBH$^+$ / VH$^+$ is large due to extensive clustering with 2-butanol; also, a large peak of butanol clusters at *m/z* 223 is observed. At ~150°C, the breaking of bonds starts and the ratio VBH$^+$ / VH$^+$ is lower than at 100°C and the peak of butanol clusters at *m/z* 223 disappears.
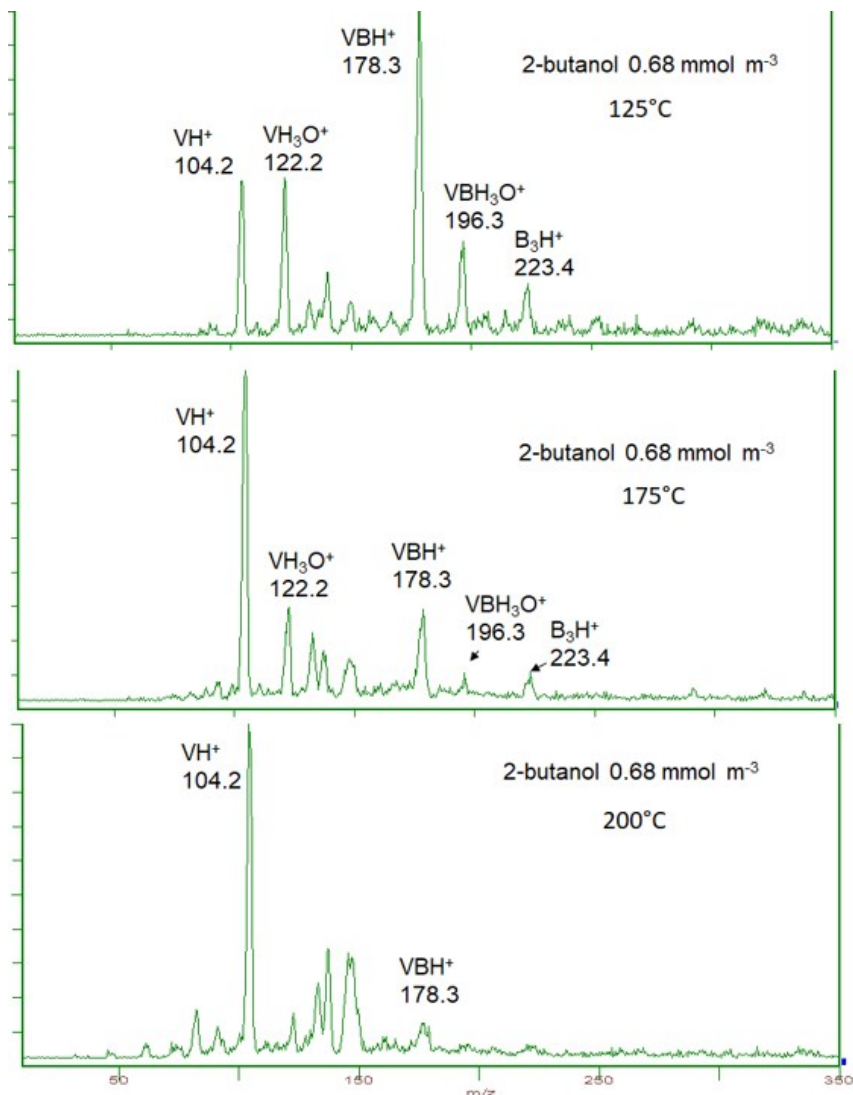
Fig. S7 Mass spectra of valinol at 100, 175 and 200°C with 0.68 mmol m^{-3} of 2-butanol in the buffer gas. Other experimental conditions were kept constant. The ratio VBH$^+$ / VH$^+$ decreases due to breaking of the clusters with increasing temperatures. Other cluster peaks such as VH$_3$O, B$_3$H$^+$ and VBH$_3$O$^+$ also decrease due to bond breaking at high temperatures.

Table S1. Mobility data for valinol (V, 104.2 Da); phenylalanine (Phe, 166.2 Da) and tryptophan (Try, 205.2 Da) **at 100°C** at different 2-butanol concentrations (B, mmol m^{-3}) in the buffer gas.

Ion	K_0	K_0 RSD	Drift time, ms	Drift time SD	n	fr	B	$\Delta K_{0,C}$ (%)	P	Ko corrected by pressure change	Uncertainty of K_0 corrected by pressure change
V	1.785	0.230	21.47	0.049	9	0	0	-	701.0	1.779	0,0063
V	1.605	0.290	23.88	0.069	11	12.5	1.7	-9.8	699.0	1.604	0,0064
V	1.563	0.200	24.52	0.049	9	25	3.4	-11.9	697.0	1.567	0,0053
V	1.523	0.040	25.16	0.010	4	50	6.8	-14.2	697.0	1.527	0,0042
Phe	1.463	0.150	26.19	0.039	7	0	0	-	699.5	1.462	0,0045
Phe	1.347	0.220	28.44	0.063	5	12.5	1.7	-7.9	699.0	1.347	0,0047
Phe	1.318	0.140	29.07	0.041	7	25	3.4	-9.6	697.0	1.322	0,0041
Phe	1.285	0.170	29.83	0.051	7	50	6.8	-11.9	697.0	1.288	0,0041
Try	1.359	0.210	28.19	0.059	8	0	0	-	699.5	1.358	0,0047
Try	1.273	0.130	30.11	0.039	10	12.5	1.7	-6.3	699.0	1.272	0,0038
Try	1.247	0.032	30.74	0.010	6	25	3.4	-8.0	697.0	1.250	0,0034
Try	1.215	0.063	31.54	0.020	6	50	6.8	-10.3	697.0	1.218	0,0034

SD: drift time standard deviation. n: number of measurements. fr: 2-butanol flow rate, µL/hr. B: 2-butanol concentrations (mmol m^{-3}) in the buffer gas. $\Delta K_{0,C}$: percent reduction in ion mobility when the buffer gas contaminant concentration was increased. P: pressure, mmHg. The values of $\Delta K_{0,C}$ were obtained as follows, for example: -9.8 = (1.604-1.779)/1.779x100; -14.2 = (1.527-1.779)/1.779x100 etc.

Table S2. Mobility data for valinol (V, 104.2 Da); phenylalanine (Phe, 166.2 Da) and tryptophan (Try, 205.2 Da) **at 150°C** at different 2-butanol concentrations (*B*, mmol m^{-3}) in the buffer gas.

Ion	K_0	K_0 RSD	Drift time, ms	SD	*n*	*fr*	*B*	$\Delta K_{0,C}$ (%)	*P*	Ko corrected by pressure change	Uncertainty of K_0 corrected by pressure change
V	1.845	0.106	18.81	0.020	5	0	0	-	698.0	1.845	0,0054
V	1.845	0.159	18.89	0.030	5	0	0	-	699.0	1.845	0,0058
V	1.783	0.205	19.54	0.040	7	12.5	1.7	-3.4	699.0	1.783	0,0061
V	1.737	0.199	20.10	0.040	5	25	3.4	-6.2	697.5	1.731	0,0058
V	1.703	0.196	20.44	0.040	7	37.5	5.1	-7.7	697.5	1.703	0,0057
V	1.677	0.144	20.82	0.030	8	50	6.8	-9.4	697.5	1.671	0,0051
Phe	1.523	0.133	22.55	0.030	6	0	0	-	699.0	1.545	0,0047
Phe	1.442	0.124	24.16	0.030	7	12.5	1.7	-6.7	699.0	1.442	0,0043
Phe	1.403	0.121	24.88	0.030	6	25	3.4	-9.4	697.5	1.399	0,0042
Phe	1.383	0.159	25.16	0.040	7	37.5	5.1	-10.5	697.5	1.383	0,0044
Phe	1.368	0.118	25.49	0.030	8	50	6.8	-11.7	697.5	1.365	0,0040
Try	1.400	0.121	24.71	0.030	6	0	0	-	699.0	1.410	0,0042
Try	1.357	0.156	25.67	0.040	7	12.5	1.7	-3.8	699.0	1.357	0,0043
Try	1.329	0.080	26.19	0.021	3	25	3.4	-5.7	697.5	1.329	0,0038
Try	1.311	0.151	26.54	0.040	8	37.5	5.1	-7.0	697.5	1.311	0,0041
Try	1.299	0.074	26.85	0.020	6	50	6.8	-8.1	697.5	1.296	0,0037

SD: drift time standard deviation. *n*: number of measurements. *fr*: 2-butanol flow rate, µL/hr. *B*: 2-butanol concentrations (mmol m^{-3}) in the buffer gas. $\Delta K_{0,C}$: percent reduction in ion mobility when the buffer gas contaminant concentration was increased. *P*: pressure, mmHg. The calculation of $\Delta K_{0,C}$ values is explained in Table S1.

Table S3. Mobility data for valinol (V, 104.2 Da); phenylalanine (Phe, 166.2 Da) and tryptophan (Try, 205.2 Da) **at 200°C** at different 2-butanol concentrations (*B*, mmol m^{-3}) in the buffer gas.

Ion	K_0	K_0 RSD	Drift time, ms	SD	N	*fr*	*B*	$\Delta K_{0,C}$ (%)	*P*	Ko corrected by pressure change	Uncertainty of K_0 corrected by pressure change
V	1.915	0.359	16.70	0.060	4	0	0	-	698.0	1.909	0,0086
V	1.904	0.060	16.79	0.010	5	12.5	1.7	-0.6	698.5	1.897	0,0053
V	1.901	0.059	16.82	0.010	5	25	3.4	-0.9	699.0	1.892	0,0053
V	1.890	0.118	16.92	0.020	5	50	6.8	-1.5	699.0	1.881	0,0056
Phe	1.589	0.099	20.12	0.020	6	0	0	-	698.0	1.584	0,0046
Phe	1.572	0.197	20.34	0.040	6	12.5	1.7	-1.1	698.5	1.566	0,0053
Phe	1.567	0.147	20.40	0.030	5	25	3.4	-1.5	699.0	1.560	0,0048
Phe	1.551	0.097	20.61	0.020	5	50	6.8	-2.5	699.0	1.544	0,0045
Try	1.448	0.136	22.08	0.030	7	0	0	-	698.0	1.444	0,0044
Try	1.440	0.090	22.20	0.020	5	12.5	1.7	-0.6	698.5	1.435	0,0041
Try	1.436	0.045	22.27	0.010	5	25	3.4	-1.0	699.0	1.429	0,0039
Try	1.431	0.224	22.35	0.050	8	50	6.8	-1.4	699.0	1.424	0,0050

SD: drift time standard deviation. *n*: number of measurements. *fr*: 2-butanol flow rate, μL/hr. *B*: 2-butanol concentrations (mmol m^{-3}) in the buffer gas. $\Delta K_{0,C}$: percent reduction in ion mobility when the buffer gas contaminant concentration was increased. *P*: pressure, mmHg. The calculation of $\Delta K_{0,C}$ values is explained in Table S1.

Table S4. Mobility data for valinol (V, 104.2 Da); phenylalanine (Phe, 166.2 Da) and tryptophan (Try, 205.2 Da) **at 250°C** at different 2-butanol concentrations (*B*, mmol m^{-3}) in the buffer gas.

Ion	K_0	K_0 RSD	Drift time, ms	SD	*n*	*fr*	*B*	$\Delta K_{0,C}$ (%)	*P*	Ko corrected by pressure change	Uncertainty of K_0 corrected by pressure change
V	1.976	0.200	14.92	0.030	5	0	0	-	693.0	1.970	0,0067
V	1.964	0.067	14.95	0.010	6	12.5	1.7	-0.2	693.0	1.966	0,0055
V	1.975	0.400	14.93	0.060	6	50	6.8	-0.1	693.0	1.969	0,0096
Phe	1.638	0.028	18.00	0.005	5	0	0	-	693.0	1.633	0,0045
Phe	1.628	0.110	18.03	0.020	6	12.5	1.7	-0.2	693.0	1.630	0,0048
Phe	1.627	0.110	18.12	0.020	6	50	6.8	-0.7	693.0	1.622	0,0048
Try	1.479	0.150	19.93	0.030	8	0	0	-	693.0	1.475	0,0046
Try	1.473	0.100	19.93	0.020	6	12.5	1.7	0.0	693.0	1.475	0,0043
Try	1.478	0.150	19.95	0.030	6	50	6.8	-0.1	693.0	1.473	0,0046

SD: drift time standard deviation. *n*: number of measurements. *fr*: 2-butanol flow rate, µL/hr. *B*: 2-butanol concentrations (mmol m^{-3}) in the buffer gas. $\Delta K_{0,C}$: percent reduction in ion mobility when the buffer gas contaminant concentration was increased. *P*: pressure, mmHg. The calculation of $\Delta K_{0,C}$ values is explained in Table S1.

Table S5. Reduction in ion mobility when the buffer gas temperature was increased from 100 to 250 °C, $\Delta K_{0,T}$, for valinol, phenylalanine and tryptophan at different 2-butanol concentrations (*) in the buffer gas.

Ion	T, °C	K_0 at different concentrations of 2-butanol in the buffer gas								$\Delta K_{0,T}$ (%)± U							
		0*	U	1.7*	U	3.4*	U	6.8*	U	0*	U	1.7*	U	3.4*	U	6.8*	U
V	100	1.779	0.006	1.604	0.006	1.567	0.005	1.527	0.004								
V	150	1.845	0.006	1.783	0.006	1.731	0.006	1.671	0.005	3.7	0.5	11.2	0.6	10.5	0.5	9.4	0.4
V	200	1.909	0.009	1.897	0.005	1.892	0.005	1.881	0.006	7.3	0.6	18.3	0.5	20.7	0.5	23.2	0.5
V	250	1.970	0.007	1.966	0.006			1.969	0.010	10.7	0.5	22.6	0.5			28.9	0.7
Phe	100	1.462	0.005	1.347	0.005	1.322	0.004	1.288	0.004								
Phe	150	1.545	0.005	1.442	0.004	1.399	0.004	1.365	0.004	5.7	0.4	7.1	0.5	5.8	0.4	6.0	0.5
Phe	200	1.584	0.005	1.566	0.005	1.560	0.005	1.544	0.004	8.3	0.4	16.3	0.5	18.0	0.5	19.9	0.5
Phe	250	1.633	0.004	1.630	0.005			1.622	0.005	11.7	0.4	21.0	0.5			25.9	0.5
Try	100	1.358	0.005	1.272	0.004	1.250	0.003	1.218	0.003								
Try	150	1.410	0.004	1.357	0.004	1.329	0.004	1.296	0.004	3.8	0.5	6.7	0.5	6.3	0.4	6.4	0.4
Try	200	1.444	0.004	1.435	0.004	1.429	0.004	1.424	0.005	6.3	0.5	12.8	0.4	14.3	0.4	16.9	0.5
Try	250	1.475	0.005	1.475	0.004			1.473	0.005	8.6	0.5	16.0	0.5			20.9	0.5

U: uncertainty. * 2-butanol concentration in mmol m^{-3}. $\Delta K_{0,T}$: percent reduction in ion mobility when the buffer gas temperature was increased; the values of $\Delta K_{0,T}$ for valinol were obtained as follows, for example: 3.7 = {(1.845-1.779)/1.779}x100; 7.3 = {(1.909-1.779)/1.779}x100 etc. Other data of this set are in tables S1-S4. The first value for $\Delta K_{0,T}$, 3.7%, is the change in mobility for valinol when 2-butanol was absent from the buffer gas and the temperature was changed from 100 to 150°C; the value of -7.3% is a similar calculation but the temperature was changed from 100 to 200°C.

Table S6. Mobility shifts for valinol (V, 104.2 Da), phenylalanine (Phe, 166.2 Da), and tryptophan (Try, 205.2 Da) at four different 2-butanol concentrations (1.7, 3.4, 5.1, and 6.8 mmol m^{-3} or 0.065, 0.131, 0.196, and 0.261 ppmv, respectively) in the buffer gas at 100, 150, 200, and 250°C.

Ion	T, °C	K_0 at different concentrations of 2-butanol in the buffer gas										$\Delta K_{0,c}$ (%)							
		0*	U	1.7*	U	3.4*	U	5,1	U	6.9*	U	1.7*	U	3.4*	U	5,1	U	6.9*	U
V	100	1.779	6.3	1.604	6.4	1.567	5.3	-	-	1.527	4.2	-9.8	0.5	-11.9	0.5	-	-	-14.2	0.4
Phe	100	1.462	4.5	1.347	4.7	1.322	4.1	-	-	1.288	4.1	-7.9	0.4	-9.6	0.4	-	-	-11.9	0.4
Try	100	1.358	4.7	1.272	3.8	1.250	3.4	-	-	1.218	3.4	-6.3	0.4	-8.0	0.4	-	-	-10.3	0.4
V	150	1.845	5.4	1.783	6.1	1.731	5.8	1.703	5.7	1.671	5.1	-3.4	0.4	-6.2	0.4	-7.7	0.4	-9.4	0.4
Phe	150	1.545	4.7	1.442	4.3	1.399	4.2	1.383	4.4	1.365	4.0	-6.7	0.4	-9.4	0.4	-10.5	0.4	-11.7	0.4
Try	150	1.410	4.2	1.357	4.3	1.329	3.8	1.311	4.1	1.296	3.7	-3.8	0.4	-5.7	0.4	-7.0	0.4	-8.1	0.4
V	200	1.909	8.6	1.897	5.3	1.892	5.3	-	-	1.881	5.6	-0.6	0.5	-0.9	0.5	-	-	-1.5	0.5
Phe	200	1.584	4.6	1.566	5.3	1.560	4.8	-	-	1.544	4.5	-1.1	0.4	-1.5	0.4	-	-	-2.5	0.4
Try	200	1.444	4.4	1.435	4.1	1.429	3.9	-	-	1.424	5.0	-0.6	0.4	-1.0	0.4	-	-	-1.4	0.5
V	250	1.970	7.0	1.966	6.0	-	-	-	-	1.969	1.0	-0.2	0.4	-	-	-	-	-0.1	0.6
Phe	250	1.633	4.0	1.630	5.0	-	-	-	-	1.622	5.0	-0.2	0.4	-	-	-	-	-0.7	0.4
Try	250	1.475	4.6	1.475	4.0	-	-	-	-	1.473	5.0	0.0	0.4	-	-	-	-	-0.1	0.4

U: uncertainty. *U:* uncertaintyx10^{-3}. $\Delta K_{0,C}$: percent reduction in ion mobility with 2-butanol concentration. *B*: 2-butanol concentrations (mmol m^{-3}) in the buffer gas. *T*: drift tube temperature. The complete data set is shown in Tables S1 to S4 (Supplementary information) including the experimental conditions, number of experiments, drift times, reduced mobilities, and statistical information from the measurements. [28] Concentrations of 2-butanol in ppmv were 0.065, 0.131, 0.196, and 0.261 for 1.7, 3.4, 5.1, and 6.8 mmol m^{-3}, respectively.