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Calibration model transfer in mid-infrared process analysis with in situ attenuated total reflectance immersion probes - Supplementary Information

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Table S1. Concentrations (% w/w) of acetone, ethanol and ethyl acetate in the calibration (samples 1 to 10) and test (samples 11 to 16) sets.

	Concentration / (% w/w)		
Sample number	Acetone	Ethanol	Ethyl acetate
1	0.0	100.0	0.0
2	100.0	0.0	0.0
3	0.0	0.0	100.0
4	50.0	50.0	0.0
5	50.0	0.0	50.0
6	0.0	49.9	50.1
7	33.3	33.4	33.3
8	65.6	17.4	17.0
9	17.0	66.0	17.0
10	17.0	17.0	66.0
11	6.0	85.0	9.0
12	26.0	61.0	13.0
13	42.0	33.0	25.0
14	83.0	10.0	7.0
15	47.0	7.0	46.0
16	11.0	18.0	71.0

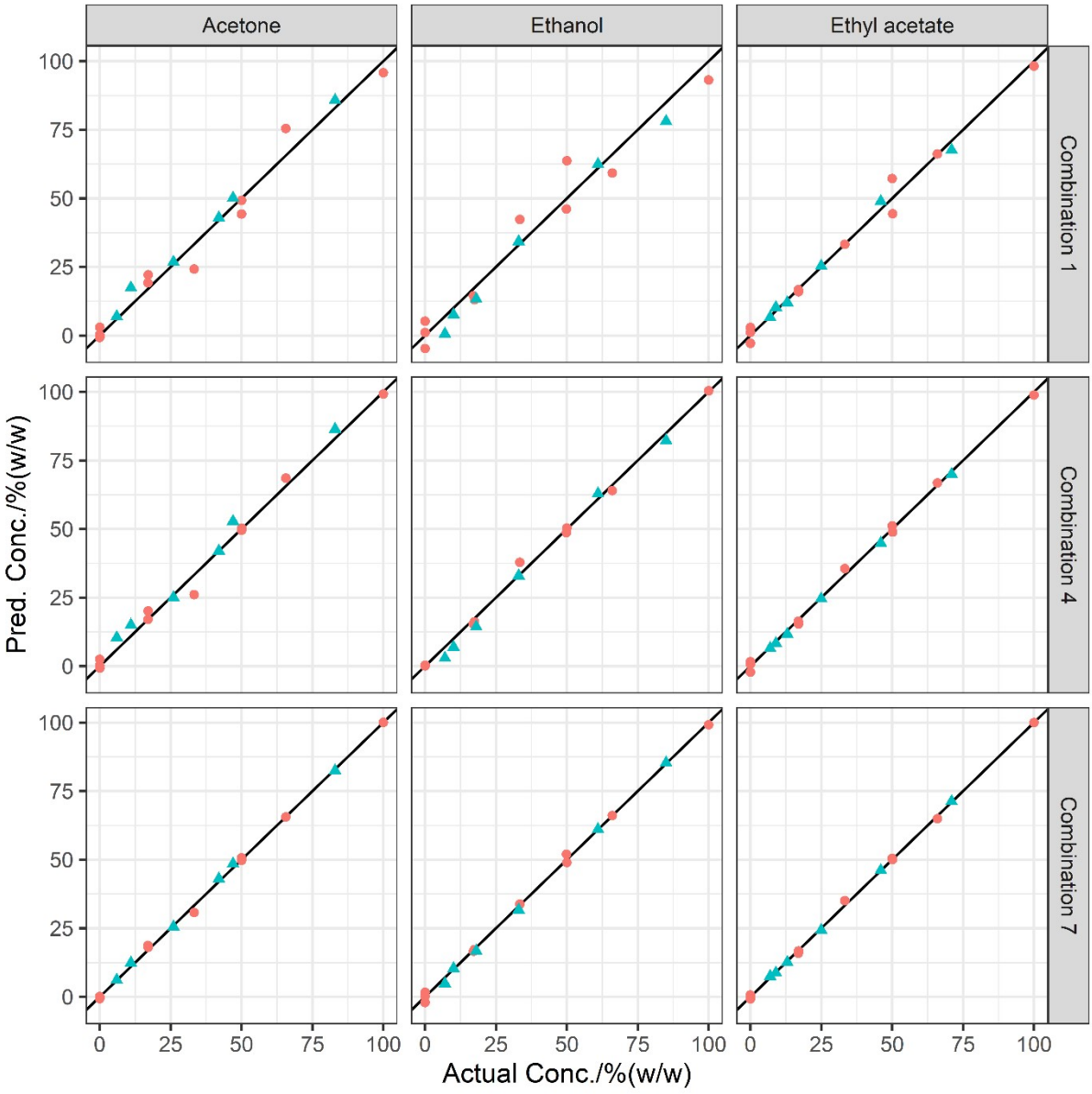

Fig. S1 Plots of actual v predicted concentration for acetone, ethanol and ethyl acetate when samples were analysed using spectrometer-probe combinations 1, 4 and 7. Red circles denotes the calibration samples, teal triangles denotes the test samples, and the solid line denotes $y = x$.

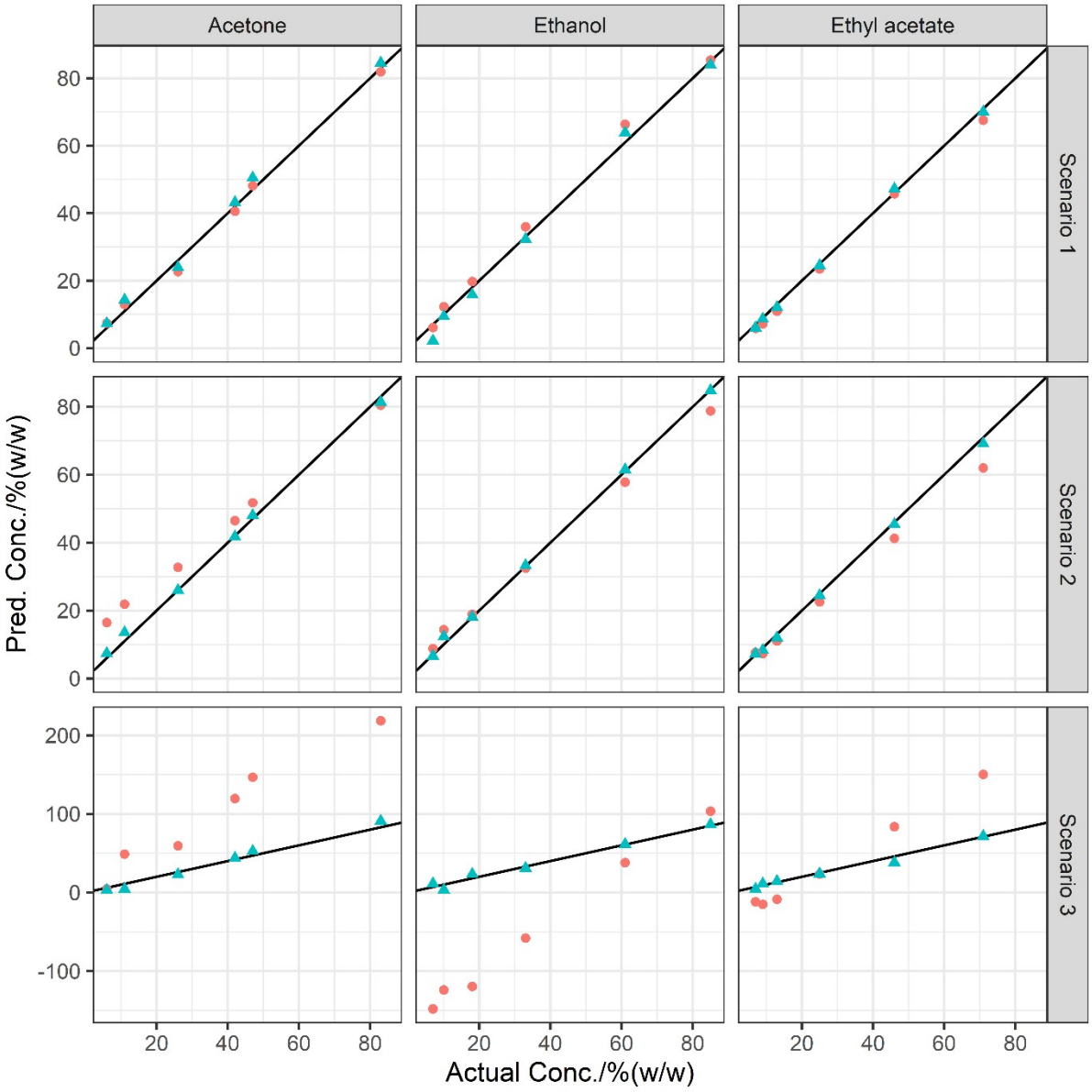

Fig. S2 Plots of actual v predicted concentration for acetone, ethanol and ethyl acetate for calibration models constructed on a primary system and used to predict the composition of test samples acquired on a secondary system without standardisation (red circles) and in conjunction with SST standardisation (teal triangles). Samples 1, 2, 3 and 7 were used for standardisation. The solid line denotes $y = x$. The spectrometer upgrade scenario 1 used the spectrometer-probe combinations 6 (primary) and 5 (secondary), the multiplexed probes scenario 2 used 7 (primary) and 6 (secondary), and the different diameter probes scenario 3 used 4 (primary) and 5 (secondary).

Table S2. RMSEP values (% w/w) for acetone, ethanol, and ethyl acetate when the calibration and test spectra were acquired using the spectrometer upgrade scenario, with and without use of DS, PDS, SST, and SST with scaling and using different subsets of standardisation samples. The primary system was the FTLA2000 spectrometer and probe 1 (spectrometer-probe combination 6), and the secondary system was the MB3000 spectrometer and probe 1 (spectrometer-probe combination 5).

Analyte	Standardisation samples	Primary test samples	Secondary test samples						
			No standardisation	DS	PDS [window size] optimised with sample 8	PDS [window size] optimised with sample 9	PDS [window size] optimised with sample 10	SST	SST with scaling
Acetone	1, 2, 3, 7	1.7	1.9	2.2	2.1 [69]	1.7 [1]	2.3 [41]	2.3	2.3
	4, 5, 6, 7			2.2	2.8 [53]	2.9 [47]	2.1 [1]	3.1	3.2
	7, 8, 9, 10			2.6	3.2 [5][a]	3.3 [7][b]	3.3 [7][c]	2.7	2.7
	2, 4, 5, 7			5.4	2.7 [3]	2.9 [33]	2.7 [7]	2.7	2.6
	1, 4, 6, 7			5.7	3.6 [1]	6.5 [35]	3.6 [1]	5.1	5.0
	3, 5, 6, 7			5.9	2.1 [17]	1.9 [1]	2.1 [35]	4.5	4.5
Ethanol	1, 2, 3, 7	1.0	2.8	2.4	2.0 [3]	2.0 [3]	2.6 [7]	2.5	2.5
	4, 5, 6, 7			1.9	2.0 [47]	2.0 [49]	2.7 [23]	2.2	2.2
	7, 8, 9, 10			2.3	2.8 [5][a]	2.6 [3][b]	2.6 [3][c]	2.5	2.5
	2, 4, 5, 7			3.7	2.4 [47]	2.4 [43]	2.7 [21]	2.4	2.3
	1, 4, 6, 7			2.4	4.3 [15]	5.1 [23]	3.6 [101]	3.8	3.8
	3, 5, 6, 7			6.2	2.0 [31]	2.0 [1]	2.2 [7]	4.0	3.9
Ethyl acetate	1, 2, 3, 7	1.5	2.0	0.9	0.9 [51]	0.6 [5]	0.9 [81]	0.8	0.8
	4, 5, 6, 7			1.9	1.9 [51]	1.3 [11]	0.9 [1]	1.6	1.6
	7, 8, 9, 10			1.8	1.4 [1][a]	1.4 [1][b]	1.4 [1][c]	1.7	1.7
	2, 4, 5, 7			2.5	1.5 [17]	1.2 [5]	1.1 [7]	1.1	1.1
	1, 4, 6, 7			4.2	2.9 [67]	1.5 [37]	1.1 [35]	1.5	1.4
	3, 5, 6, 7			1.6	1.3 [5]	0.8 [31]	1.2 [35]	1.5	1.5

[a] PDS window size was optimised with sample 1
[b] PDS window size was optimised with sample 2
[c] PDS window size was optimised with sample 3

Table S3. RMSEP values (% w/w) for acetone, ethanol and ethyl acetate when the calibration and test spectra were acquired using the multiplexed probes scenario, with and without use of DS, PDS, SST, and SST with scaling and using different subsets of standardisation samples. The primary system was the FTLA2000 spectrometer and probe 2 (spectrometer-probe combination 7), and the secondary system was the FTLA2000 spectrometer and probe 1 (spectrometer-probe combination 6).

Analyte	Standardisation samples	Primary test samples	Secondary test samples						
			No standardisation	DS	PDS [window size] (optimised with sample 8)	PDS [window size] (optimised with sample 9)	PDS [window size] (optimised with sample 10)	SST	SST with scaling
Acetone	1, 2, 3, 7	1.0	7.3	1.4	1.5 [3]	1.5 [43]	1.3 [101]	1.4	1.4
	4, 5, 6, 7			3.9	2.7 [5]	2.3 [3]	1.9 [1]	2.4	2.2
	7, 8, 9, 10			2.1	1.1 [7][a]	1.3 [3][b]	1.1 [21][c]	1.9	1.8
	2, 4, 5, 7			3.7	2.2 [7]	1.6 [51]	1.4 [33]	1.8	1.7
	1, 4, 6, 7			3.6	1.9 [1]	3.7 [95]	2.2 [31]	1.9	1.8
	3, 5, 6, 7			2.1	1.9 [1]	1.9 [3]	2.2 [101]	2.0	2.1
Ethanol	1, 2, 3, 7	1.2	3.5	1.0	0.8 [1]	0.9 [3]	0.8 [1]	1.0	1.0
	4, 5, 6, 7			1.7	0.9 [11]	1.0 [1]	2.0 [65]	1.3	1.3
	7, 8, 9, 10			0.9	0.8 [15][a]	0.8 [13][b]	1.1 [5][c]	0.8	0.8
	2, 4, 5, 7			1.8	1.5 [7]	0.9 [93]	1.5 [7]	1.1	1.0
	1, 4, 6, 7			2.5	1.1 [1]	1.6 [3]	1.1 [1]	1.4	1.3
	3, 5, 6, 7			2.4	1.1 [9]	1.4 [47]	1.1 [1]	1.3	1.3
Ethyl acetate	1, 2, 3, 7	0.4	4.4	1.6	1.1 [3]	1.0 [7]	1.1 [3]	1.0	1.0
	4, 5, 6, 7			3.0	2.6 [11]	2.3 [71]	1.7 [1]	1.7	1.6
	7, 8, 9, 10			1.4	0.9 [19][a]	1.2 [1][b]	0.9 [21][c]	1.0	1.0
	2, 4, 5, 7			3.9	1.8 [7]	1.5 [33]	1.8 [1]	1.8	1.7
	1, 4, 6, 7			4.0	3.1 [69]	3.1 [83]	1.3 [31]	1.4	1.2
	3, 5, 6, 7			2.3	1.7 [1]	1.7 [55]	1.7 [1]	1.4	1.3

[a] PDS window size was optimised with sample 1

[b] PDS window size was optimised with sample 2

[c] PDS window size was optimised with sample 3

Table S4. RMSEP values (% w/w) for acetone, ethanol and ethyl acetate when the calibration and test spectra were acquired using the different probe diameter scenario (2.7 to 12 mm), with and without use of DS, PDS, SST, and SST with scaling and using different subsets of standardisation samples. The primary system was the MB3000 spectrometer and probe 3 (spectrometer-probe combination 4), and the secondary system was the MB3000 spectrometer and probe 1 (spectrometer-probe combination 5).

Analyte	Standardisation samples	Primary test samples	Secondary test samples						
			No standardisation	DS	PDS [window size] (optimised with sample 8)	PDS [window size] (optimised with sample 9)	PDS [window size] (optimised with sample 10)	SST	SST with scaling
Acetone	1, 2, 3, 7	3.7	78.4	3.0	3.0 [5]	3.1 [3]	3.1 [3]	5.2	3.0
	4, 5, 6, 7			6.2	3.2 [5]	2.9 [3]	6.0 [91]	9.7	8.4
	7, 8, 9, 10			6.8	2.2 [1][a]	1.9 [3][b]	2.2 [1][c]	5.8	5.5
	2, 4, 5, 7			3.3	5.6 [1]	2.3 [45]	3.6 [81]	14.1	6.3
	1, 4, 6, 7			6.8	4.4 [83]	3.9 [1]	5.9 [7]	14.1	10.7
	3, 5, 6, 7			8.0	3.7 [11]	4.5 [33]	4.7 [5]	15.0	12.2
Ethanol	1, 2, 3, 7	2.9	108.1	3.0	3.5 [5]	3.0 [1]	3.5 [5]	4.0	2.6
	4, 5, 6, 7			6.2	3.1 [1]	4.8 [3]	3.1 [1]	10.0	7.3
	7, 8, 9, 10			5.2	2.1 [3][a]	2.1 [5][b]	2.0 [1][c]	3.0	3.4
	2, 4, 5, 7			3.1	4.3 [1]	2.8 [71]	4.3 [1]	10.0	4.8
	1, 4, 6, 7			8.0	4.4 [1]	5.8 [101]	4.8 [55]	10.3	7.4
	3, 5, 6, 7			5.7	5.9 [1]	5.5 [101]	5.9 [1]	13.2	8.6
Ethyl acetate	1, 2, 3, 7	0.9	39.0	1.3	1.1 [35]	1.3 [21]	1.6 [79]	3.6	1.0
	4, 5, 6, 7			2.0	1.9 [65]	2.3 [29]	2.4 [27]	6.0	2.7
	7, 8, 9, 10			1.8	2.2 [101][a]	1.8 [45][b]	2.0 [41][c]	3.0	1.6
	2, 4, 5, 7			3.6	1.2 [35]	0.5 [23]	2.9 [47]	7.7	2.1
	1, 4, 6, 7			2.8	1.1 [1]	1.5 [35]	1.8 [37]	12.6	5.4
	3, 5, 6, 7			2.8	3.9 [35]	1.5 [53]	2.5 [81]	4.6	2.9

[a] PDS window size was optimised with sample 1
[b] PDS window size was optimised with sample 2
[c] PDS window size was optimised with sample 3