Electronic Supplementary Information (ESI) for JAAS article:

Quantification of C, H, N and O in polymers using WDXRF scattering spectra and PLS regression depending on the spectral resolution

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Mold

The mold used for the production of unsaturated polyester resin (UP) and epoxy resins (EP) samples is displayed in Fig. S 1. This mold was produced by Computerized Numerical Control (CNC) machinery. The mold cavities are visible when the lid is open, as shown in Fig. S 1(a).

(a) (b)

Fig. S 1 Aluminium mold used to cast EP and UP samples, 40 mm diameter cavities, a) mold open, b) mold closed.

Cross-validation procedure

At first, the complete data set was split randomly into a training set (67%, 56 samples) and a testing set (33%, 28 samples). The training set was used to perform cross-validation (CV) according to the scheme in Fig. S 2. CV was used to determine the optimal number of partial least squares (PLS) components, i.e. the model's complexity. This was achieved by a random splitting of training data into segments, which are also called folds. In this study, leave-one-out (LOO) CV was performed, thus the number of segments was equal to the number of samples in the training set. In each fold, all samples but one was used as a sub-training set to fit the model. The excluded sample from each fold was used as a validation set or validation sample in LOO CV, respectively. The validation sample was predicted by the trained model. For each fold, the residuals of predicted and reference values are calculated. The mean square error (MSE) of the validation samples were calculated. To determine to optimal number of PLS components, another round with higher number of PLS components was performed. Thereafter, the MSE of CV was plotted against the number of PLS components to find the optimum number of PLS components.

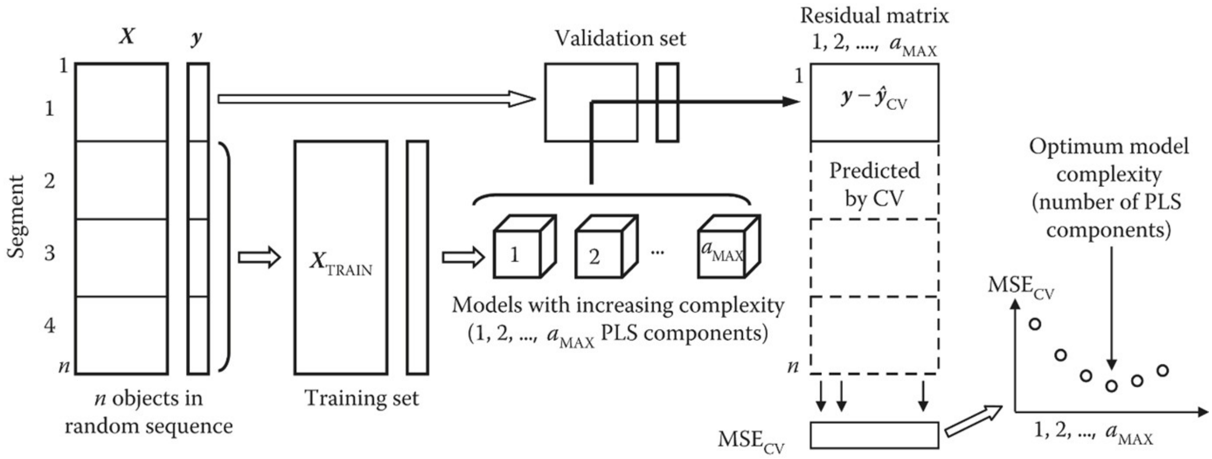

Fig. S 2 Cross-validation, e.g. with 4 splits, used for the estimation of optimal number of PLS components. From: Introduction to multivariate statistical analysis in chemometrics, K. Varmuza, P. Filzmoser (© 2009, CRC Press). Reproduced by permission of Taylor & Francis Group.

Recovery plots at low concentration levels for CHNO predictions

In Fig. S 3, the CHNO predictions in the low concentrations range below 10 wt.% are depicted. In this concentrations range, as for the total concentration range, the low spectral resolution showed the smallest deviations from the reference data. Especially concerning N concentrations, the low spectral resolution performed best for training and testing data.

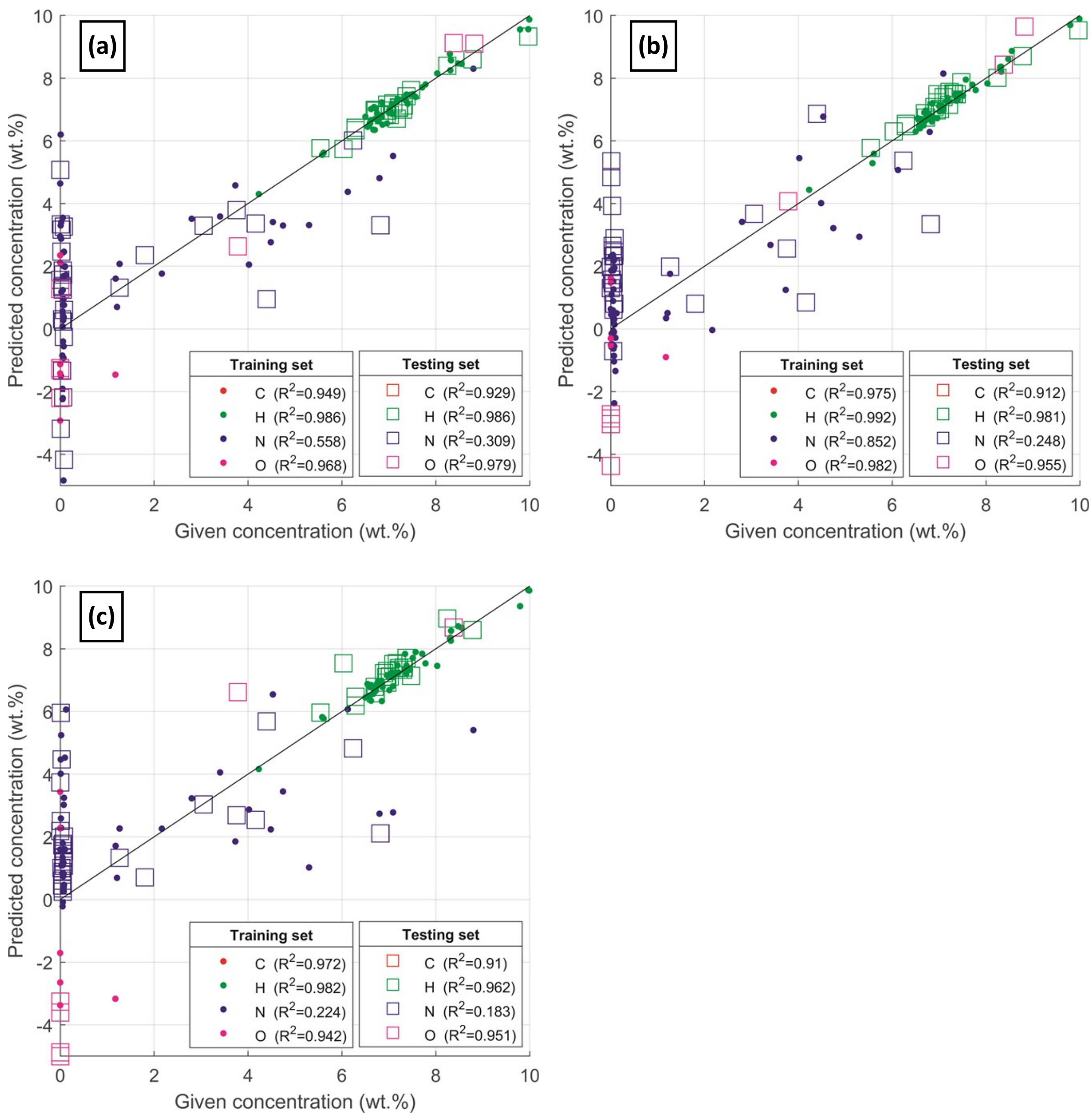

Fig. S 3 CHNO predictions from PLS models in low concentrations range, a) low spectral resolution, b) medium spectral resolution, c) high spectral resolution, Carbon absent in this range, R² in legends correspond to predictions on the full concentration range as a compare.

Elemental analysis of plastic samples

Tab. S 1: Elemental analysis of plastic samples C, H, and N concentrations, O balanced; split into training set samples (table head) and testing set samples (table tail) indicated by the horizontal bar.

Sample	Element concentration (wt.%)			
	C	H	N	O
UP 1	68.68 ± 0.11	6.62 ± 0.01	0.08 ± 0.01	24.63
UP 2	65.45 ± 0.23	6.58 ± 0.01	0.06 ± 0.01	27.92
PUR 1	64.21 ± 0.33	8.31 ± 0.04	6.13 ± 0.01	21.36
PS 1	91.75 ± 0.47	8.32 ± 0.04	0 ± 0.01	0
EP 1	66.79 ± 1.23	7.38 ± 0.01	2.8 ± 0.01	23.04
UP 3	72.53 ± 0.31	7.19 ± 0.04	0.06 ± 0.01	20.23
PA 1	66.07 ± 0.17	7.51 ± 0.01	10.87 ± 0.03	15.55
UP 4	67.17 ± 0.2	6.7 ± 0.01	0.05 ± 0.01	26.08
UP 5	65.08 ± 0.69	6.6 ± 0.05	0.07 ± 0.01	28.26
UP 6	69.91 ± 0.21	6.71 ± 0.01	0.03 ± 0.01	23.37
TPU 1	62.5 ± 0.04	7.07 ± 0.01	3.73 ± 0.03	26.71
UP 7	69.19 ± 0.06	6.85 ± 0.01	0.08 ± 0.01	23.89
UP 8	71.23 ± 0.15	7.36 ± 0.04	0.08 ± 0.01	21.34
UP 9	69.29 ± 0.25	6.71 ± 0.01	0.06 ± 0.01	23.95
EP 2	67.51 ± 0.18	7.09 ± 0.04	1.18 ± 0.03	24.23
PMMA 1	59.26 ± 0.18	8.03 ± 0.03	0.01 ± 0	32.7
UP 10	70.8 ± 0.21	7.07 ± 0.01	0.05 ± 0.04	22.09
UP 11	69.29 ± 0.63	6.69 ± 0.01	0.06 ± 0.02	23.98
PA 2	63.23 ± 0.08	9.8 ± 0.13	12.09 ± 0.02	14.89
UP 12	67.6 ± 0.37	6.6 ± 0.03	0.06 ± 0.03	25.75
PA 3	72.82 ± 0.09	9.99 ± 0.03	7.09 ± 0.01	10.1
UP 13	68.04 ± 0.1	6.5 ± 0.01	0.06 ± 0.01	25.41
UP 14	69.92 ± 0.29	6.75 ± 0.01	0.08 ± 0	23.26
EP 3	67.1 ± 0.27	7.21 ± 0.01	1.27 ± 0.01	24.43
UP 15	67.86 ± 0.04	6.67 ± 0	0.08 ± 0	25.39
PET 1	61.47 ± 0.2	4.23 ± 0	0 ± 0	34.3
POM 1	40.55 ± 0.04	6.85 ± 0.01	0.1 ± 0.02	52.5
PUR 2	65.12 ± 0.58	8.55 ± 0.07	4.02 ± 0.01	22.31
PC 1	74.69 ± 0.58	5.61 ± 0.02	0.02 ± 0.01	19.68
UP 16	65.96 ± 0.07	6.55 ± 0.01	0.05 ± 0.01	27.45
UP17	69.32 ± 0.04	6.96 ± 0.01	0.07 ± 0.03	23.65
PUR 3	62.72 ± 0.13	8.48 ± 0.02	3.41 ± 0.01	25.41
UP 18	70.49 ± 0.19	7.01 ± 0.01	0.06 ± 0	22.45
PA 4	63.37 ± 0.2	9.97 ± 0.07	12.18 ± 0.05	14.48
ABS 1	87.26 ± 0.58	7.78 ± 0.01	5.3 ± 0.03	0
UP 19	69.29 ± 0.12	6.72 ± 0	0.07 ± 0.01	23.93
PP 1	85.13 ± 0.18	14.25 ± 0.48	0.02 ± 0.02	0
UP 20	69.96 ± 0.1	6.85 ± 0.01	0.07 ± 0.01	23.12
UP 21	70.89 ± 0.08	7.17 ± 0.02	0.06 ± 0.01	21.89
PE 1	85.22 ± 0.11	13.48 ± 0	0.13 ± 0.01	1.18
UP 22	70.32 ± 0.97	7.35 ± 0.02	0.02 ± 0.01	22.33
PE 2	85.42 ± 0.18	13.96 ± 0.23	0.01 ± 0.01	0

Sample	Element concentration (wt.%)			
	C	H	N	O
PC 2	73.67 ± 0.53	5.58 ± 0.04	0.1 ± 0	20.66
EP 4	66.87 ± 0.06	7.37 ± 0.01	2.17 ± 0.02	23.6
UP 23	71.72 ± 0.15	7.4 ± 0.01	1.21 ± 0.06	19.68
ABS 2	85.2 ± 0.5	7.71 ± 0.04	6.8 ± 0.04	0
UP 24	68.69 ± 0.25	6.78 ± 0.01	0.06 ± 0.01	24.48
UP 25	68.1 ± 0.17	6.62 ± 0.01	0.07 ± 0.01	25.21
PA 5	65.7 ± 0.45	7.45 ± 0.04	10.67 ± 0.08	16.18
EP 5	66.61 ± 0.04	7.57 ± 0	4.49 ± 0.04	21.34
PUR 4	64.59 ± 0.02	8.3 ± 0.03	4.53 ± 0.1	22.59
UP 26	69.25 ± 0.01	6.87 ± 0.01	0.05 ± 0.03	23.84
PA 6	68.42 ± 0.14	11.2 ± 0.1	8.8 ± 0.01	11.58
PA 7	64.28 ± 0.36	10.45 ± 0.02	11.09 ± 0.06	14.18
PUR 5	66.11 ± 0.1	8.33 ± 0.01	4.75 ± 0.05	20.82
UP 27	75.49 ± 0.14	7 ± 0.01	0.05 ± 0.01	17.46
PA 8	72.21 ± 0.31	12.15 ± 0.03	6.82 ± 0.03	8.82
UP 28	68.87 ± 0.57	7.22 ± 0.04	0.07 ± 0.01	23.85
UP 29	75.67 ± 0.15	6.97 ± 0.04	0.08 ± 0.01	17.3
UP 30	69.99 ± 0.33	6.95 ± 0.04	0.04 ± 0.01	23.03
UP 31	70.45 ± 0.37	6.72 ± 0	0.06 ± 0.04	22.78
PA 9	63.1 ± 0.12	9.97 ± 0.02	12.15 ± 0.03	14.78
UP 32	68.92 ± 0.08	7.1 ± 0.01	0.08 ± 0.01	23.91
UP 33	71.82 ± 0.42	7.02 ± 0.03	0.07 ± 0.02	21.1
UP 34	64.74 ± 0.08	6.29 ± 0.01	0.06 ± 0.02	28.92
EP 6	66.49 ± 0.04	7.48 ± 0.01	3.76 ± 0.02	22.28
PE 3	85.17 ± 0.36	14.63 ± 0.51	0.03 ± 0.01	0
PA 10	73.88 ± 0.51	11.5 ± 0.12	6.24 ± 0.03	8.38
UP 35	70.64 ± 0.67	7.38 ± 0.02	1.8 ± 0	20.19
UP 36	72.54 ± 0.03	7.31 ± 0.04	0.06 ± 0.01	20.1
UP 37	71.42 ± 0.32	7.32 ± 0.01	1.27 ± 0.02	20
PUR 6	63.57 ± 0.22	8.78 ± 0.08	3.06 ± 0.04	24.6
PE 4	85.74 ± 0.14	14.24 ± 0.45	0.01 ± 0.01	0
UP 38	69.48 ± 0.25	6.7 ± 0.02	0.05 ± 0.01	23.79
UP 39	66.61 ± 0.13	6.29 ± 0	0.03 ± 0.01	27.08
PP 2	85.79 ± 0.08	14.33 ± 0.49	0.01 ± 0.01	0
UP 40	71.66 ± 0.35	7.17 ± 0.04	0.08 ± 0.03	21.1
PR 1	73.93 ± 0.07	6.04 ± 0.02	4.4 ± 0.07	15.65
UP 41	65.24 ± 0	6.97 ± 0.02	0.08 ± 0.02	27.72
PE 5	85.83 ± 0.1	14.11 ± 0.11	0 ± 0	0
PBT 1	64.85 ± 0.06	5.54 ± 0	0 ± 0	29.61
UP 42	70.13 ± 0.03	7.21 ± 0.01	0.04 ± 0	22.62
ABS 3	83.81 ± 0.02	8.25 ± 0.01	4.17 ± 0.01	3.78
UP 43	69.65 ± 0.08	6.9 ± 0.01	0.06 ± 0.01	23.4

CHNO predictions from WDXRF spectra

Tab. S 2: CHNO predictions from WDXRF spectra for 3 used spectral resolutions, split into training set samples (table head) and testing set samples (table tail) indicated by the horizontal bar.

	Spectral resolution | Element concentration (wt.%)											
Sample	**Low**				**Medium**				**High**			
	C	**H**	**N**	**O**	**C**	**H**	**N**	**O**	**C**	**H**	**N**	**O**
UP 1	65.95	7.02	1.67	25.37	68.05	6.70	0.31	24.95	70.07	6.34	0.40	23.21
UP 2	65.18	6.48	2.01	26.38	65.57	6.45	0.43	27.58	65.56	6.48	0.35	27.63
PUR 1	63.19	8.25	4.37	24.20	64.04	8.35	5.07	22.54	64.14	8.36	6.07	21.43
PS 1	89.68	8.58	4.64	-2.93	89.81	8.37	2.31	-0.52	91.14	8.26	2.28	-1.71
EP 1	65.84	7.48	3.51	23.15	65.45	7.50	3.41	23.62	65.77	7.47	3.23	23.52
UP 3	72.19	7.34	0.77	19.68	72.64	7.37	-0.06	20.01	70.85	7.47	1.80	19.85
PA 1	68.01	7.49	8.28	16.25	67.88	7.44	8.61	16.14	67.53	7.71	3.56	21.19
UP 4	68.62	6.35	-1.91	26.94	67.07	6.64	0.35	25.95	66.39	6.65	1.19	25.79
UP 5	65.50	6.58	0.95	27.00	66.99	6.40	-0.10	26.73	65.40	6.78	0.34	27.48
UP 6	68.58	6.70	1.18	23.55	68.63	6.70	-0.48	25.14	68.15	6.75	1.08	24.02
TPU 1	62.92	7.18	4.58	25.35	62.69	7.10	1.25	28.96	62.85	7.25	1.85	28.06
UP 7	70.72	6.81	0.37	22.10	70.86	6.78	-0.55	22.90	69.36	6.98	0.26	23.39
UP8	71.87	7.29	-0.55	21.35	71.94	7.41	-2.37	22.94	70.87	7.33	3.02	18.78
UP 9	68.36	7.04	-0.40	24.98	67.19	6.96	1.26	24.57	68.60	6.75	1.61	23.05
EP 2	66.36	7.16	1.60	24.87	68.02	6.95	0.34	24.67	67.85	6.81	1.71	23.65
PMMA 1	54.99	8.15	6.20	30.64	58.07	7.83	1.86	32.19	59.34	7.46	4.01	29.21
UP 10	71.97	6.86	-0.85	22.01	70.22	7.10	2.36	20.33	70.78	7.09	0.83	21.30
UP 11	67.16	7.08	3.55	22.23	67.56	6.90	1.52	24.03	69.15	6.69	-0.09	24.25
PA 2	66.81	9.55	6.32	17.24	64.22	9.70	11.46	14.63	67.73	9.36	2.67	20.15
UP 12	66.55	6.55	1.67	25.25	67.74	6.48	0.22	25.57	67.39	6.51	0.78	25.35
PA 3	74.37	9.87	5.52	10.15	72.98	9.89	8.15	8.93	74.32	9.86	2.78	12.93
UP 13	65.80	6.77	1.24	26.21	68.33	6.29	-0.11	25.51	67.80	6.45	0.26	25.51
UP 14	69.60	6.87	0.76	22.76	70.28	6.71	0.14	22.87	69.63	6.90	0.47	23.00
EP 3	66.39	7.32	2.08	24.20	66.67	7.26	1.76	24.30	67.68	7.24	2.27	22.81
UP 15	69.21	6.36	2.46	22.00	69.04	6.49	1.95	22.54	67.52	6.57	3.25	22.70
PET 1	59.26	4.30	2.95	33.63	59.41	4.44	0.63	35.63	61.11	4.16	1.59	33.28
POM 1	42.94	6.76	2.00	48.32	42.69	6.61	-0.28	50.97	39.65	6.85	4.53	49.01
PUR 2	67.16	8.45	2.05	22.31	64.25	8.87	5.45	21.41	64.95	8.67	2.87	23.47
PC 1	74.91	5.62	2.88	16.69	74.87	5.59	1.09	18.52	73.47	5.78	2.28	18.55
UP 16	67.01	6.45	0.08	26.48	65.69	6.72	2.31	25.31	65.39	6.88	1.13	26.61
UP17	71.67	6.56	-4.84	26.58	70.58	6.72	-0.86	23.55	68.54	7.15	1.18	23.13
PUR 3	62.41	8.47	3.59	25.52	62.24	8.61	2.68	26.43	61.50	8.72	4.06	25.69
UP 18	68.31	7.00	2.44	22.26	68.96	6.94	2.17	21.94	71.03	6.68	1.56	20.75
PA 4	66.56	9.56	8.27	15.55	63.23	10.08	9.33	17.30	64.80	9.87	5.23	20.00
ABS 1	86.78	7.80	3.31	2.10	87.82	7.62	2.94	1.63	89.16	7.53	1.02	2.27
UP 19	67.97	7.04	0.28	24.69	70.58	6.72	-0.86	23.55	67.84	6.66	0.74	24.78
PP 1	83.53	13.92	3.40	-1.13	84.30	14.03	-0.15	1.48	83.24	13.90	5.24	-2.65
UP 20	65.23	7.23	1.69	25.86	65.70	7.19	2.20	24.92	70.07	6.33	0.37	23.26
UP 21	70.69	7.25	0.42	21.63	70.96	7.28	-0.63	22.35	70.94	7.24	0.81	20.99
PE 1	85.73	13.74	1.72	-1.46	86.26	13.83	0.50	-0.90	82.55	14.29	6.06	-3.17

UP 22	71.66	7.32	-1.50	22.47	71.18	7.49	-0.57	21.84	69.16	7.84	2.59	20.38
PE 2	83.50	14.30	3.30	-1.42	85.68	13.83	0.45	-0.30	84.83	13.80	4.47	-3.37
PC 2	74.21	5.56	1.98	18.33	76.26	5.29	-1.34	19.85	72.66	5.82	1.60	19.98
EP 4	65.64	7.47	1.76	25.10	66.54	7.28	-0.04	26.18	66.51	7.20	2.26	24.03
UP 23	73.13	7.19	0.70	18.97	72.58	7.32	0.51	19.57	72.81	7.35	0.69	19.13
ABS 2	85.17	7.71	4.81	2.35	84.36	7.79	6.29	1.61	85.97	7.84	2.74	3.44
UP 24	69.08	6.62	-2.21	26.50	67.98	6.85	1.87	23.32	67.68	6.96	1.09	24.27
UP 25	67.91	6.66	-0.93	26.35	67.57	6.64	-1.04	26.82	67.27	6.84	0.83	25.06
PA 5	67.91	7.47	5.18	19.20	67.70	7.51	8.14	16.70	69.37	7.33	2.84	20.46
EP 5	68.26	7.40	2.77	21.58	65.87	7.96	4.01	22.15	66.13	7.90	2.24	23.71
PUR 4	63.36	8.78	3.41	24.38	64.18	8.36	6.77	20.68	64.51	8.33	6.54	20.62
UP 26	70.86	6.52	-2.24	24.86	69.75	6.76	0.89	22.62	70.12	6.78	-0.22	23.32
PA 6	67.83	10.97	8.30	12.78	68.06	11.04	10.19	10.63	70.13	10.82	5.41	13.52
PA 7	67.22	9.92	6.99	15.78	65.35	10.13	10.91	13.58	67.25	9.95	3.94	18.75
PUR 5	67.08	8.57	3.30	21.04	67.23	8.21	3.22	21.34	65.87	8.57	3.45	22.08
UP 27	76.00	6.89	0.56	16.54	75.26	7.11	0.59	17.02	74.69	7.10	1.34	16.86
PA 8	75.99	11.41	3.31	9.10	75.65	11.18	3.34	9.65	76.77	10.91	2.11	10.04
UP 28	69.27	7.05	-2.18	25.83	66.82	7.56	1.46	24.13	68.57	7.39	1.33	22.70
UP 29	75.26	7.16	3.26	14.33	71.68	7.49	0.80	20.00	72.96	7.29	1.08	18.66
UP 30	70.40	6.85	-1.34	24.08	69.38	6.97	1.45	22.20	69.37	7.10	0.60	22.93
UP 31	68.75	6.96	1.37	22.92	69.32	6.75	1.17	22.78	71.69	6.58	0.35	21.39
PA 9	67.73	9.33	7.69	15.24	68.29	9.53	8.20	13.99	66.83	10.11	4.71	18.28
UP 32	69.33	7.20	0.61	22.84	68.04	7.39	2.45	22.11	67.34	7.52	2.01	23.12
UP 33	71.65	6.83	1.74	19.80	70.34	7.02	2.00	20.64	70.29	7.12	1.35	21.24
UP 34	64.13	6.34	1.86	27.71	63.64	6.47	2.32	27.62	64.03	6.47	0.88	28.65
EP 6	65.43	7.62	3.79	23.14	64.45	7.87	2.56	25.07	68.35	7.13	2.69	21.83
PE 3	83.87	13.99	3.17	-1.32	85.17	13.68	3.92	-3.04	84.95	13.58	4.47	-3.26
PA 10	73.74	11.01	6.01	9.12	75.17	10.91	5.37	8.43	75.19	11.17	4.83	8.68
UP 35	72.15	7.43	2.35	18.06	71.68	7.49	0.80	20.00	71.06	7.71	0.70	20.49
UP 36	73.67	7.00	0.24	19.08	71.22	7.51	0.61	20.61	71.02	7.33	1.78	19.85
UP 37	71.77	7.13	1.31	19.77	69.96	7.51	1.99	20.52	69.96	7.40	1.33	21.28
PUR 6	63.43	8.60	3.29	24.64	62.75	8.71	3.67	24.84	65.29	8.60	3.03	23.04
PE 4	84.63	13.97	3.34	-2.21	84.71	14.05	5.35	-4.37	84.50	14.15	5.96	-4.87
UP 38	68.58	6.99	1.33	23.10	68.79	6.88	2.50	21.84	69.10	6.79	1.73	22.40
UP 39	65.54	6.42	2.47	25.61	64.97	6.54	1.58	26.93	66.50	6.19	1.01	26.34
PP 2	87.88	13.70	-3.18	1.28	83.36	14.22	4.85	-2.72	87.23	13.59	2.51	-3.61
UP 40	75.32	6.71	-4.17	22.11	70.87	7.48	2.89	18.75	70.15	7.54	1.54	20.74
PR 1	77.48	5.74	0.95	15.96	75.04	6.30	6.86	11.94	69.96	7.54	5.68	16.87
UP 41	66.38	6.97	-0.25	26.90	64.54	7.23	2.33	25.90	66.26	6.92	1.21	25.62
PE 5	85.49	13.89	1.57	-1.25	87.85	13.42	1.30	-2.85	87.87	13.15	3.74	-5.00
PBT 1	62.28	5.77	5.07	26.97	62.31	5.78	1.98	30.00	60.36	5.97	2.19	31.55
UP 42	71.30	7.07	0.31	21.31	70.42	7.15	2.65	19.80	69.44	7.33	0.45	22.76
ABS 3	85.58	8.40	3.36	2.63	87.04	8.01	0.84	4.07	81.81	8.97	2.54	6.61
UP 43	69.29	6.82	1.25	22.66	67.41	7.08	-0.71	26.20	67.64	7.22	0.25	24.87