S.1 Average R²P of the compared methods in the analysis of ash content

Target domain training set size	R²P of direct modeling	R²P of fine-tuning of source domain model	R²P of fine-tuning of cross-domain model	R²P of HTr-LIBS
2	-1.0406	-0.5346	-0.5314	0.6450
3	-0.6993	0.2126	0.2401	0.5995
4	-0.1881	0.2602	0.3117	0.4699
5	0.2703	0.3238	0.4723	0.5849
6	0.3543	0.2360	0.5092	0.6012
7	0.4906	0.5142	0.5906	0.7580
8	0.5335	0.3419	0.6468	0.7956
9	0.5685	0.7083	0.6907	0.8222
10	0.6805	0.7144	0.7759	0.7955
11	0.7250	0.7178	0.6938	0.8439
12	0.7556	0.7949	0.7248	0.8593
13	0.7561	0.7609	0.7701	0.8571
14	0.7680	0.7237	0.8308	0.8625
15	0.7394	0.8698	0.8491	0.8720
16	0.7644	0.7970	0.8504	0.8525
17	0.7777	0.7947	0.8048	0.8870
18	0.7766	0.7590	0.8097	0.8762
19	0.8105	0.8361	0.8227	0.9029

S.2 Average RMSEP of the compared methods in the analysis of ash content

Target domain training set size	RMSEP of direct modeling (wt.%)	RMSEP of fine-tuning of source domain model (wt.%)	RMSEP of fine-tuning of cross-domain model (wt.%)	RMSEP of HTr-LIBS (wt.%)
2	9.1765	7.7218	8.1149	3.9094
3	8.4603	5.8365	5.6909	4.0782
4	7.1709	5.5987	5.4597	4.7944
5	5.5924	5.3291	4.7112	4.1170
6	5.2548	5.7426	4.6106	4.1462
7	4.6028	4.4764	4.2132	3.2492
8	4.3749	5.1085	3.9208	2.9784
9	4.1930	3.4245	3.6421	2.7642
10	3.7070	3.5285	3.1227	2.9720
11	3.4536	3.4489	3.6570	2.6096
12	3.2630	2.9610	3.4204	2.4765
13	3.2612	3.0194	3.1577	2.5045
14	3.1711	3.3879	2.7167	2.4415
15	3.3464	2.2737	2.5653	2.3706

16	3.1918	2.9129	2.5392	2.5261
17	3.0935	2.8530	2.8990	2.2191
18	3.1042	2.6633	2.8701	2.3136
19	2.8823	2.5699	2.7878	2.0588

S.3 Average MAEP of the compared methods in the analysis of ash content

Target domain training set size	MAEP of direct modeling (wt.%)	MAEP of fine-tuning of source domain model (wt.%)	MAEP of fine-tuning of cross-domain model (wt.%)	MAEP of HTr-LIBS (wt.%)
2	7.1262	6.3819	6.6945	3.2366
3	6.8122	4.8225	4.4820	3.2557
4	5.5418	4.3279	4.3084	3.9851
5	4.1034	3.9701	3.5671	3.1373
6	3.6860	3.8449	3.6773	3.0934
7	3.5846	3.5535	3.0831	2.5560
8	3.3893	3.8162	3.0223	2.3265
9	3.1556	2.5595	2.6623	2.1994
10	2.8718	2.5891	2.3797	2.4459
11	2.7145	2.3292	2.6909	1.9977
12	2.5171	1.9388	2.2813	1.9283
13	2.5393	2.4212	2.1309	1.9815
14	2.4836	1.8752	2.0485	1.9237
15	2.5502	1.3290	1.9010	1.8166
16	2.4393	1.5107	1.8652	1.9356
17	2.3339	1.5312	1.9999	1.6588
18	2.3253	1.9825	1.9536	1.7140
19	2.1387	1.7117	1.8687	1.6055

S.4 Average R^2P of the compared methods in the analysis of volatile matter content

Target domain training set size	R^2P of direct modeling	R^2P of fine-tuning of source domain model	R^2P of fine-tuning of cross-domain model	R^2P of HTr-LIBS
2	-1.9798	-0.5504	-0.1010	0.4454
3	-0.2440	-0.1177	0.2780	0.4921
4	-0.2963	0.2520	0.3641	0.6127
5	0.0965	0.2957	0.6170	0.7050
6	0.2796	0.6384	0.7313	0.7791
7	0.6098	0.2228	0.7870	0.8137
8	0.6364	0.5065	0.8161	0.8225
9	0.7537	0.5858	0.8695	0.8757
10	0.5891	0.4567	0.7710	0.8014

11	0.7348	0.3718	0.7999	0.8011
12	0.7046	0.5628	0.8226	0.8376
13	0.7557	0.3514	0.8042	0.8750
14	0.8390	0.5529	0.8111	0.8447
15	0.8613	0.7669	0.8206	0.8901
16	0.8939	0.6762	0.8991	0.9140
17	0.9330	0.8287	0.9221	0.9342
18	0.9378	0.9325	0.9470	0.9489
19	0.9440	0.9309	0.9497	0.9627

S.5 Average RMSEP of the compared methods in the analysis of volatile matter content

Target domain training set size	RMSEP of direct modeling (wt.%)	RMSEP of fine-tuning of source domain model (wt.%)	RMSEP of fine-tuning of cross-domain model (wt.%)	RMSEP of HTr-LIBS (wt.%)
2	14.1647	10.0288	8.4446	6.0974
3	8.9981	8.6316	6.6631	5.8097
4	8.9547	7.0847	6.3375	5.1080
5	7.5011	6.7883	4.6972	4.3787
6	6.6596	4.9482	4.2836	3.7686
7	5.1551	7.3418	3.7763	3.6052
8	4.7533	5.6642	3.4292	3.4388
9	4.0456	5.1968	2.9645	2.8875
10	5.2414	5.9353	3.8139	3.5264
11	4.2394	6.4220	3.5847	3.6114
12	4.4348	5.4075	3.4194	3.2723
13	3.9880	6.5464	3.5958	2.7841
14	3.2434	5.2784	3.5221	3.1652
15	3.0194	3.7133	3.3031	2.6488
16	2.6758	4.5032	2.6180	2.3533
17	2.1593	3.4454	2.2921	2.0878
18	2.0845	1.9525	1.8879	1.8822
19	1.9764	2.1149	1.8693	1.6083

S.6 Average MAEP of the compared methods in the analysis of volatile matter content

Target domain training set size	MAEP of direct modeling (wt.%)	MAEP of fine-tuning of source domain model (wt.%)	MAEP of fine-tuning of cross-domain model (wt.%)	MAEP of HTr-LIBS (wt.%)
2	12.2574	8.2785	6.3143	4.5663
3	7.2387	6.8265	5.2255	4.4279
4	7.3288	5.3523	4.4332	3.5759
5	5.7140	5.2975	3.3819	3.4131

6	4.8847	3.8101	3.1876	2.9200
7	3.9298	5.4331	2.7645	2.7385
8	3.6163	3.7928	2.5723	2.6024
9	3.0248	3.4494	2.2100	2.2230
10	3.7598	4.2633	2.6150	2.5431
11	3.0159	4.3499	2.4389	2.4964
12	3.1259	3.5035	2.2926	2.2323
13	2.8346	4.5369	2.3854	1.8737
14	2.3987	2.9130	2.3453	2.1045
15	2.2715	2.3116	2.0866	1.8142
16	1.9201	2.8494	1.7528	1.6016
17	1.6381	1.9266	1.5877	1.4941
18	1.5345	1.1988	1.3317	1.3428
19	1.4626	1.2115	1.3822	1.2224