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PLS Regression-Assisted LIBS for Simultaneous Quantitative Analysis of five REEs and TREO in Rare Earth Ores

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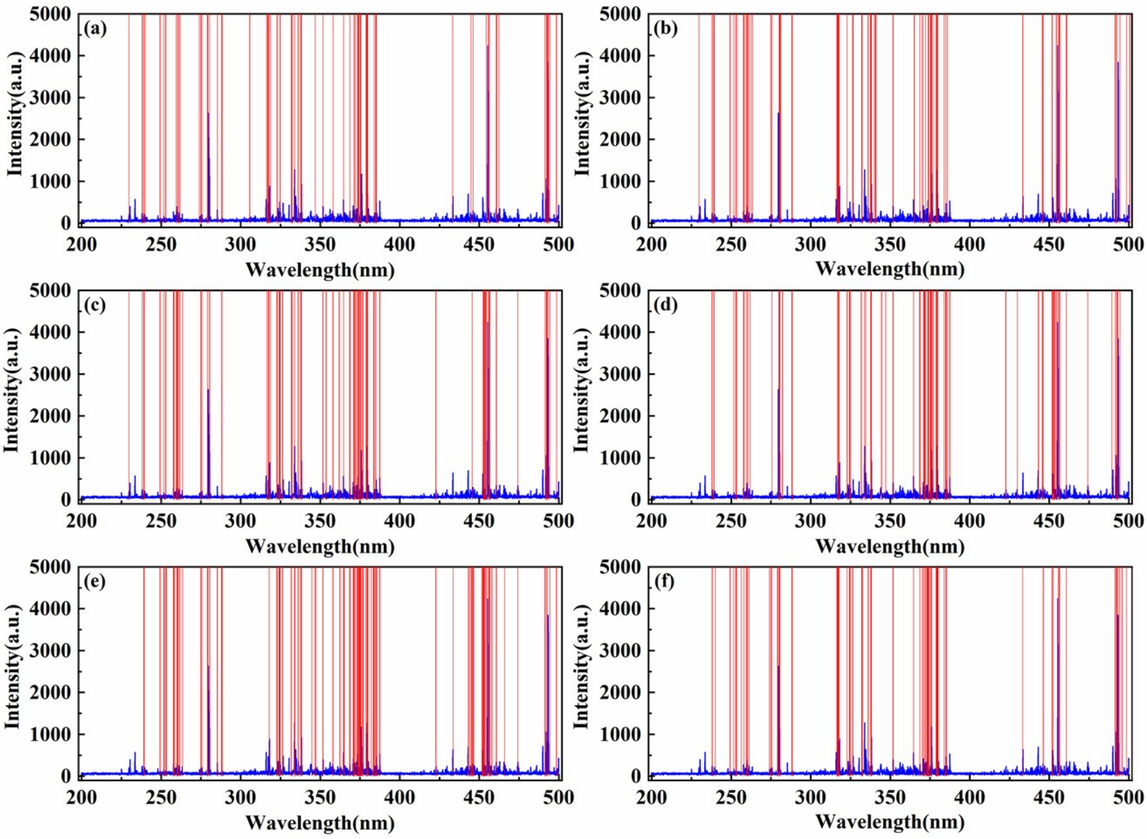

Fig. S1 Variable Selection Based on CARS [(a) La; (b) Ce; (c) Pr; (d) Nd; (e) Sm; (f) TREO].

Table S1 Prediction results of the PLS correction model based on different smoothing points (3-25) of D1st

REEs	**Smoothing points**	**LV**	**R^2_{cv}**	**MRE_{cv}**	**REEs**	**Smoothing points**	**LV**	**R^2_{cv}**	**MRE_{cv}**
La	3	3	0.8006	0.4087	**Ce**	3	3	0.7628	0.3333
	5	3	0.7975	0.4075		5	3	0.7600	0.3314
	7	3	0.7951	0.4077		7	3	0.7587	0.326
	9	12	0.9109	0.4061		**9**	**3**	**0.7584**	**0.3203**
	11	12	0.9096	0.4004		11	3	0.7557	0.3225
	13	12	0.9070	0.4073		13	3	0.7506	0.3251
	15	**12**	**0.9133**	**0.3866**		15	11	0.9051	0.3275
	17	12	0.9165	0.3900		17	11	0.9058	0.3304
	19	11	0.9124	0.4036		19	11	0.9026	0.3398
	21	11	0.9105	0.4282		21	3	0.7535	0.3467
	23	11	0.9108	0.4429		23	3	0.7541	0.3562
	25	11	0.9129	0.4339		25	3	0.7532	0.3609
Pr	3	8	0.8626	0.3391	**Nd**	3	8	0.8555	0.3244
	5	9	0.8790	0.3269		5	9	0.8738	0.3154
	7	10	0.8843	0.3217		7	10	0.8795	0.3028
	9	10	0.8904	0.3148		9	10	0.8858	0.2966
	11	12	0.8906	0.3067		11	10	0.8831	0.2871
	13	3	0.6818	0.3150		13	10	0.8772	0.2938
	15	**11**	**0.8949**	**0.3066**		15	10	0.8830	0.2893
	17	9	0.8864	0.3092		**17**	**10**	**0.8821**	**0.2859**
	19	11	0.8906	0.3134		19	10	0.8780	0.2983
	21	11	0.8904	0.3164		21	9	0.8776	0.3124
	23	9	0.8834	0.3310		23	9	0.8776	0.3190
	25	11	0.8914	0.3312		25	9	0.8767	0.3216
Sm	3	8	0.8462	0.3454	**TREO**	3	3	0.7720	0.3326
	5	9	0.8666	0.3302		5	3	0.7692	0.3310
	7	10	0.8757	0.3100		7	3	0.7677	0.3268
	9	10	0.8820	0.3017		**9**	**3**	**0.7672**	**0.3227**
	11	10	0.8792	0.2902		11	3	0.7645	0.3278
	13	10	0.8734	0.2941		13	3	0.7595	0.3306
	15	10	0.8792	0.286		15	11	0.9064	0.3311
	17	**10**	**0.8785**	**0.2835**		17	11	0.9076	0.3312
	19	10	0.8754	0.2904		19	11	0.9044	0.3396
	21	10	0.8746	0.3117		21	3	0.7625	0.3499
	23	10	0.8740	0.3195		23	3	0.7633	0.3547
	25	10	0.8743	0.3207		25	3	0.7627	0.3595

Table S2 Prediction results of the PLS correction model based on different smoothing points (3-25) of D2nd

REEs	Smoothing points	LV	R^2_{cv}	MRE_{cv}	REEs	Smoothing points	LV	R^2_{cv}	MRE_{cv}
La	3	3	0.8028	0.4126	Ce	3	3	0.7641	0.3394
	5	3	0.8000	0.4087		5	3	0.7613	0.339
	7	3	0.7982	0.4019		7	3	0.7603	0.3333
	9	**13**	**0.9021**	**0.3937**		**9**	**3**	**0.7630**	**0.3212**
	11	3	0.7986	0.4060		11	3	0.7627	0.3257
	13	3	0.7924	0.4151		13	3	0.7563	0.3237
	15	11	0.9041	0.4075		15	3	0.7540	0.3232
	17	13	0.9052	0.4229		17	3	0.7573	0.3324
	19	13	0.8983	0.4148		19	3	0.7604	0.3306
	21	3	0.7963	0.4175		21	3	0.7602	0.3412
	23	3	0.7947	0.4194		23	3	0.7596	0.3373
	25	3	0.7967	0.4158		25	9	0.8944	0.3322
Pr	3	12	0.8623	0.3526	Nd	3	12	0.8548	0.3414
	5	11	0.8714	0.3381		5	11	0.8649	0.3265
	7	9	0.8801	0.3321		7	16	0.8719	0.3181
	9	**10**	**0.8866**	**0.3265**		9	10	0.8816	0.3098
	11	9	0.8850	0.3116		**11**	**12**	**0.8789**	**0.2989**
	13	3	0.6866	0.3329		13	10	0.8644	0.3232
	15	11	0.8878	0.3135		15	9	0.8809	0.3005
	17	11	0.8836	0.3220		17	9	0.8729	0.3025
	19	9	0.8780	0.3280		19	9	0.8727	0.3158
	21	11	0.8772	0.3443		21	8	0.8617	0.3216
	23	9	0.8799	0.3351		23	8	0.8651	0.3159
	25	9	0.8813	0.3102		25	9	0.8762	0.2992
Sm	3	13	0.8471	0.3584	TREO	3	3	0.7735	0.3374
	5	11	0.8591	0.3432		5	3	0.7706	0.3368
	7	16	0.8672	0.3304		7	3	0.7695	0.3315
	9	10	0.8771	0.3211		**9**	**3**	**0.7719**	**0.3211**
	11	12	0.8740	0.3137		11	3	0.7717	0.3266
	13	10	0.8603	0.3312		13	3	0.7652	0.3247
	15	**12**	**0.8757**	**0.3110**		15	3	0.7631	0.3250
	17	11	0.8719	0.3225		17	3	0.7664	0.3348
	19	10	0.8659	0.3255		19	3	0.7695	0.3320
	21	11	0.8669	0.3397		21	3	0.7691	0.3409
	23	9	0.8681	0.3363		23	3	0.7685	0.3363
	25	9	0.8693	0.3178		25	3	0.7689	0.3367

Table S3 The prediction results of the PLS correction model based on different parameters of WT (wavelet basis functions db2-db14, coif1-5; decomposition levels 1-15).

REEs	Wavelet basis function	Decomposition levels	R^2_{cv}	MRE_{cv}
La	db2	10	0.9722	0.3191
	db3	15	0.9719	0.2968
	db4	11	0.9719	0.3338
	db5	6	0.9731	0.3089
	db6	13	0.9732	0.2974
	db7	15	0.9706	0.2825
	db8	12	0.9737	0.3201
	db9	7	0.9718	0.2979
	db10	9	0.9702	0.3086
	db11	10	0.9716	0.3125
	db12	6	0.9717	0.2917
	db13	**8**	**0.9712**	**0.2773**
	db14	15	0.9717	0.2884
	coif1	10	0.9719	0.3114
	coif2	13	0.9719	0.314
	coif3	15	0.9729	0.3127
	coif4	14	0.9734	0.3221
	coif5	3	0.9686	0.3192
Ce	db2	10	0.9662	0.2561
	db3	12	0.9612	0.2933
	db4	1	0.9572	0.3075
	db5	15	0.9666	0.2541
	db6	14	0.9674	0.2519
	db7	10	0.9639	0.2552
	db8	9	0.9676	0.2628
	db9	**12**	**0.9672**	**0.2263**
	db10	9	0.9653	0.2531
	db11	14	0.9664	0.2535
	db12	9	0.9679	0.2475
	db13	9	0.9650	0.2545
	db14	10	0.9643	0.2501
	coif1	13	0.9632	0.2766
	coif2	13	0.9643	0.2811
	coif3	13	0.9655	0.2681
	coif4	12	0.9675	0.2583
	coif5	12	0.9679	0.2632
Pr	db2	12	0.9538	0.2521
	db3	12	0.946	0.2926
	db4	6	0.9482	0.3012
	db5	10	0.9547	0.2544
	db6	11	0.9572	0.2465

	db7	14	0.9534	0.2567
	db8	9	0.9575	0.2508
	db9	**10**	**0.9574**	**0.2048**
	db10	15	0.9564	0.2378
	db11	14	0.9553	0.2654
	db12	13	0.9606	0.2245
	db13	11	0.9563	0.2488
	db14	11	0.9537	0.2592
	coif1	5	0.949	0.2623
	coif2	12	0.9532	0.2718
	coif3	11	0.9543	0.2573
	coif4	15	0.9554	0.2546
	coif5	6	0.9537	0.2568
Nd	db2	12	0.9487	0.2454
	db3	5	0.9376	0.2719
	db4	6	0.9435	0.2875
	db5	13	0.9498	0.2472
	db6	11	0.9526	0.2436
	db7	13	0.949	0.2525
	db8	9	0.9528	0.2445
	db9	**12**	**0.9537**	**0.1978**
	db10	12	0.953	0.2295
	db11	14	0.95	0.2607
	db12	13	0.957	0.2173
	db13	11	0.952	0.2406
	db14	11	0.9494	0.2576
	coif1	5	0.9443	0.2522
	coif2	12	0.948	0.2659
	coif3	11	0.9491	0.2528
	coif4	6	0.9461	0.25
	coif5	6	0.9495	0.2485
Sm	db2	12	0.9436	0.2637
	db3	4	0.9294	0.3057
	db4	3	0.9338	0.3144
	db5	13	0.9448	0.2701
	db6	11	0.9484	0.2648
	db7	12	0.9443	0.2727
	db8	9	0.9482	0.2622
	db9	**11**	**0.95**	**0.2168**
	db10	13	0.949	0.254
	db11	14	0.9453	0.2817
	db12	13	0.9531	0.2357
	db13	11	0.9486	0.2563
	db14	11	0.9455	0.2812

	coif1	5	0.938	0.2782
	coif2	12	0.9428	0.2841
	coif3	11	0.9438	0.2756
	coif4	6	0.941	0.2725
	coif5	6	0.9449	0.2714
TREO	db2	10	0.9673	0.2546
	db3	12	0.9635	0.2823
	db4	1	0.9593	0.2986
	db5	10	0.9679	0.2443
	db6	13	0.9686	0.255
	db7	10	0.9652	0.2501
	db8	10	0.9686	0.2655
	db9	**12**	**0.9678**	**0.2342**
	db10	9	0.9659	0.2616
	db11	15	0.9677	0.2517
	db12	14	0.9703	0.2467
	db13	9	0.9661	0.2509
	db14	15	0.9658	0.2458
	coif1	5	0.963	0.2722
	coif2	12	0.9656	0.2805
	coif3	12	0.9673	0.2605
	coif4	12	0.9692	0.2527
	coif5	12	0.9693	0.2543

Table S4 Results of PLS correction model constructed by single and hybrid preprocessing.

REEs	Parameter	LV	Model	R^2_{cv}	MRE_{CV}
La	/	13	Raw	0.911	0.5357
	15	12	D1st	0.9133	0.3866
	9	13	D2nd	0.9021	0.3937
	db13/11	11	wt	0.9556	0.3523
	/	4	Nor	0.8892	0.4808
	/	8	MSC	0.9587	0.3528
	/	8	SNV	0.9679	0.3425
	db13/8	**10**	**SNV-WT**	**0.9712**	**0.2773**
	db13/11	10	WT-SNV	0.9697	0.3063
	15-db8/5	9	D1st-WT	0.9356	0.3436
	db13/11-3	13	WT-D1st	0.9405	0.3525
Ce	/	10	Raw	0.8965	0.4451
	9	3	D1st	0.7584	0.3203
	9	3	D2nd	0.763	0.3212
	db13/13	12	wt	0.9436	0.2675
	/	4	Nor	0.9211	0.398
	/	6	MSC	0.9361	0.3064
	/	6	SNV	0.9569	0.2459
	db9/12	**9**	**SNV-WT**	**0.9672**	**0.2263**
	db13/13	7	WT-SNV	0.9472	0.2805
	9-db6/2	10	D1st-WT	0.9293	0.2769
	db13/13-21	15	WT-D1st	0.9441	0.2334
Pr	/	10	Raw	0.8786	0.4073
	15	11	D1st	0.8949	0.3066
	9	1	D2nd	0.8813	0.3102
	db13/15	10	wt	0.9222	0.2691
	/	7	Nor	0.9158	0.3181
	/	6	MSC	0.8959	0.3545
	/	6	SNV	0.9315	0.2748
	db9/10	**11**	**SNV-WT**	**0.9574**	**0.2048**
	db13/15	12	WT-SNV	0.9512	0.262
	15-db6/6	10	D1st-WT	0.9222	0.2586
	db13/15-9	15	WT-D1st	0.9232	0.2299
Nd	/	10	Raw	0.8713	0.3848
	17	10	D1st	0.8821	0.2859
	11	12	D2nd	0.8789	0.2989
	db10/3	11	wt	0.9110	0.2634
	/	8	Nor	0.9081	0.3232
	/	8	MSC	0.8909	0.3649
	/	6	SNV	0.9193	0.2980
	db9/12	**12**	**SNV-WT**	**0.9537**	**0.1978**
	db10/3	6	WT-SNV	0.9090	0.2788

	17-db6/6	11	D1st-WT	0.9102	0.2558
	db10/3-13	10	WT-D1st	0.9068	0.2339
Sm	/	10	Raw	0.8640	0.3984
	17	10	D1st	0.8785	0.2835
	15	12	D2nd	0.8757	0.311
	db11/15	9	wt	0.9172	0.2666
	/	8	Nor	0.9000	0.3319
	/	8	MSC	0.8779	0.3963
	/	8	SNV	0.9159	0.3273
	db9/11	**11**	**SNV-WT**	**0.9500**	**0.2168**
		6	WT-SNV	0.8958	0.3111
	17-db6/12	10	D1st-WT	0.9061	0.2568
	db11/15-13	10	WT-D1st	0.9026	0.2608
TREO	/	10	Raw	0.8991	0.4433
	9	3	D1st	0.7672	0.3227
	9	3	D2nd	0.7719	0.3211
	db13/15	9	wt	0.9433	0.2711
	/	4	Nor	0.9198	0.3959
	/	6	MSC	0.9412	0.2925
	/	6	SNV	0.9590	0.2456
	db9/12	**10**	**SNV-WT**	**0.9678**	**0.2342**
	db13/15	10	WT-SNV	0.9609	0.2764
	9-db6/2	12	D1st-WT	0.9245	0.2786
	db13/15-25	15	WT-D1st	0.9451	0.2516

Table S5 Results of PLS correction model constructed by optimal preprocessing combined with different variable selection methods.

REEs	Parameter	LV	Model	Number of variables	R^2_{cv}	MRE_{cv}
La	/	13	Raw	5784	0.9110	0.5357
	6; 3	10	SNV-WT-siPLS	2892	0.9648	0.3188
	0.9	12	SNV-WT-VIP	361	0.9706	0.3391
	30; 0.7; 2	4	SNV-WT-PSO	247	0.9479	0.2941
	/	13	SNV-WT-MI	400	0.9690	0.3233
	N=90, K=5	**10**	**SNV-WT-CARS**	**72**	**0.9981**	**0.0615**
Ce	/	10	Raw	5784	0.8965	0.4451
	6; 3	5	SNV-WT-siPLS	2892	0.9385	0.2571
	0.9	6	SNV-WT-VIP	341	0.9351	0.2681
	30; 0.7; 2	8	SNV-WT-PSO	229	0.9456	0.2780
	/	7	SNV-WT-MI	400	0.9396	0.2720
	N=95, K=3	**15**	**SNV-WT-CARS**	**117**	**0.9992**	**0.0340**
Pr	/	10	Raw	5784	0.8786	0.4073
	6; 3	9	SNV-WT-siPLS	2892	0.9419	0.2600
	0.8	11	SNV-WT-VIP	338	0.9409	0.2850
	30; 0.7; 2	5	SNV-WT-PSO	250	0.9298	0.2595
	/	12	SNV-WT-MI	400	0.9251	0.2820
	N=55, K=5	**16**	**SNV-WT-CARS**	**125**	**0.9987**	**0.0490**
Nd	/	10	Raw	5784	0.8713	0.3848
	6; 3	9	SNV-WT-siPLS	2892	0.9361	0.2676
	0.9	11	SNV-WT-VIP	3856	0.9352	0.2799
	30; 0.7; 2	5	SNV-WT-PSO	1444	0.9224	0.2495
	/	9	SNV-WT-MI	337	0.9097	0.2813
	N=55, K=3	**19**	**SNV-WT-CARS**	**125**	**0.9986**	**0.0451**
Sm	/	10	Raw	5784	0.8640	0.3984
	6; 3	7	SNV-WT-siPLS	2892	0.9159	0.3548
	1.0	6	SNV-WT-VIP	3856	0.9275	0.2755
	30; 0.7; 2	6	SNV-WT-PSO	1444	0.9281	0.2813
	/	15	SNV-WT-MI	341	0.9299	0.2961
	N=55, K=3	**16**	**SNV-WT-CARS**	**167**	**0.9962**	**0.0766**
TREO	/	10	Raw	5784	0.8991	0.4433
	6; 3	5	SNV-WT-siPLS	2892	0.9399	0.2785
	0.9	6	SNV-WT-VIP	341	0.9395	0.2762
	30; 0.7; 2	5	SNV-WT-PSO	247	0.9526	0.2132
	/	10	SNV-WT-MI	400	0.9529	0.2785
	N=90, K=3	**17**	**SNV-WT-CARS**	**112**	**0.9991**	**0.0453**