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Electronic Supplementary Information

Matrix Complexity Effect on Platinum Group Metals Analysis using Inductively Coupled Plasma Optical Emission Spectroscopy

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Electronic Supplementary Information Content

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Supplemental Methods Description

3.5. Effect of instrument precision and stability

The proportion of measurements with analysis %RSD over 10% is presented in Figure S1. For platinum, 265.945 nm was the most precise wavelength, with only 7.8% of measurements exceeding 10 %RSD. For rhodium, 343.489 nm was the more precise option with 10 % of measurements deemed imprecise. Ru 349.894 nm was the most imprecise of the studied wavelengths with 15.7 % of measurements. Interestingly, Os 225.585 nm was the most precise wavelength, with 3.8 %. This occurred because the memory effect caused an overestimation of the concentration, and generally, the %RSD tends to be lower at higher concentrations, because of the high signal to background ratio generated by the resulting higher peak intensities. As a whole, the effect of interferents on measurement precision does not appear to be as influential as the effect on measurement accuracy, as outlined in the main body of the paper.

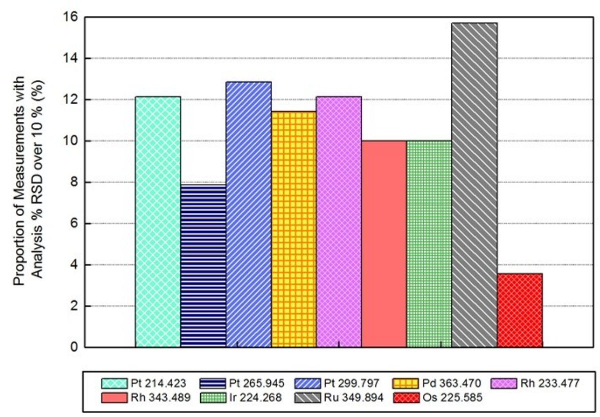


Figure S1. Proportion of ICP-OES replicates reading standard deviation for all matrix test solutions, which exceed a precision limit of 10% (n = 140).

3.6. Relative effect of matrix parameters – Empirical model building

A summary of the fitted parameters is presented in Table S1, and correlation plots for these models are given in Figure S2. An important note is that because these systems are expected to be non-linear and chaotic, the resulting models are not intended to be predictive in nature, but instead are intended to indicate the relative importance of various factors on the measurement error.

For the platinum wavelengths, the absolute error for Pt 214.423 nm appears to show a heavy negative bias, as confirmed by the distributions in section 3.3. The number of interferents had a large negative impact on the absolute error. The remaining primary test factors and the combination of the number and individual concentration of interferents appeared to have a relatively equal, and moderately important effect on the absolute error; however, the quadratic effect of the PGM concentration was relatively small in comparison. Both Pt 265.945 nm and Pt 299.797 nm show less negative baseline bias, and in general, all the test factors contributed to less error. In both cases, the PGM concentration was a main contributor to the error, with a larger negative error occurring at higher concentrations, and the other parameters having a smaller contribution, except for the number of interferents, which had a large negative impact on error for Pt 299.797 nm. Between these two wavelengths, Pt 265.945 nm appeared to be less sensitive to changes in the matrix complexity than Pt 299.797 nm, but more sensitive to non-linear effects of PGM concentration. The relatively high R^2 for these models indicates that these matrix effects can explain an important proportion (71 – 79%) of the observed variance in the absolute error, thus these matrix parameters have an important impact on the error and must be considered when trying to quantify PGMs with ICP-OES.

Pd 363.470 nm shows a negative bias in the error, and each of the matrix parameters appeared to have a relatively equal importance, except the number of interferents, which had a larger effect; however, this model is highly inadequate for explaining the variance in the error data (R^2 = 23%). The observed error is thus primarily determined by other factors that were not considered in the model, such as interference by individual species, specific combinations of interferents, and/or random error. For palladium quantification, these matrix parameters are thus not a major consideration for measurement accuracy.

Rh 343.489 nm appeared to be a considerably more reliable option for rhodium quantification than Rh 233.477 nm. The latter had a strong negative bias (β_0 = – 10.16 mg/L), and each of the studied matrix parameters have a strong effect on the error, with large factor parameters, and a relatively strong correlation to these parameters (R^2 = 78 %). In contrast, Rh 343.489 nm measurement error appeared to be relatively weakly affected by the studied factor parameters (low magnitude). Furthermore, the observed error is not strongly correlated to these factors (R^2 = 15%), which indicates that for Rh 343.489 nm, quantification is not strongly affected by the studied matrix parameters.

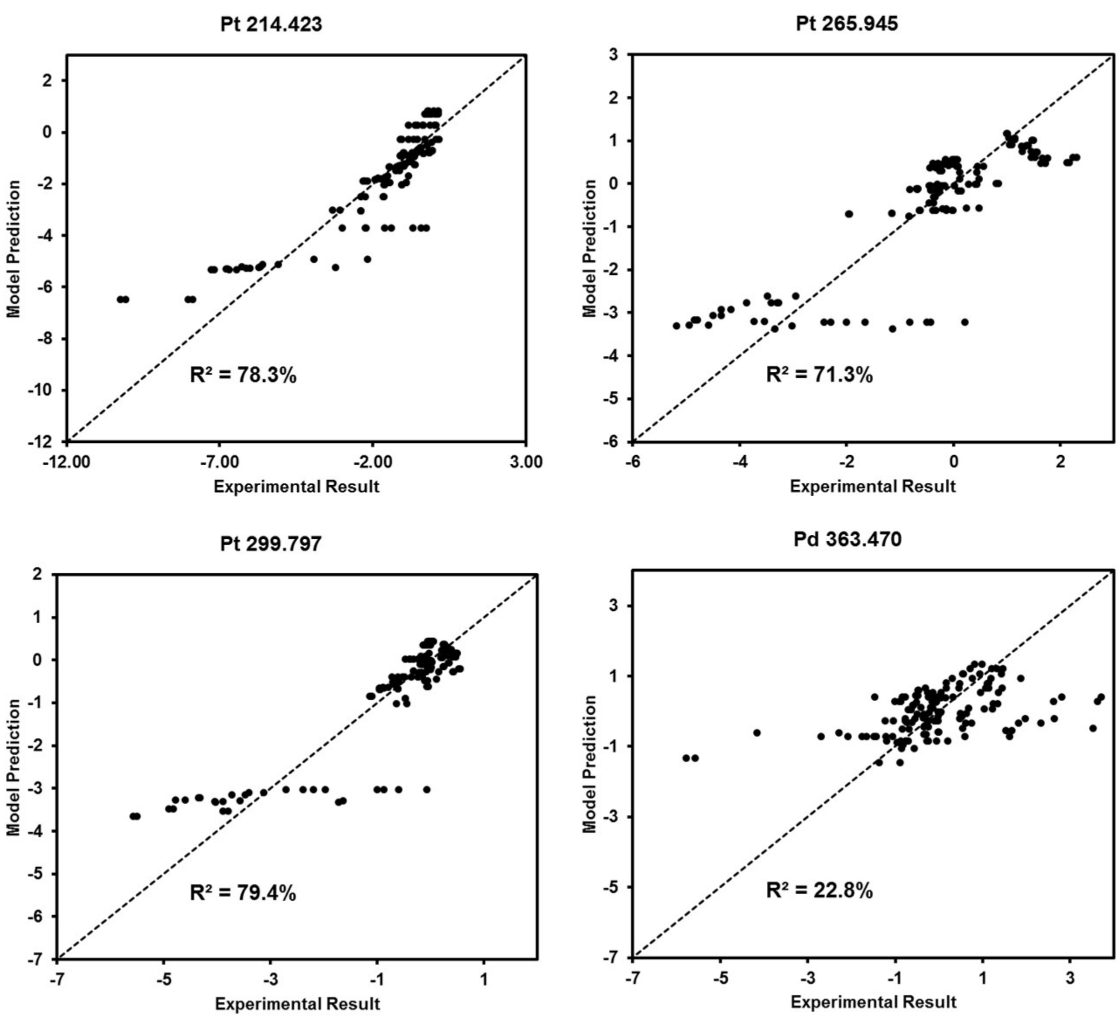
The error for Ir 224.268 nm measurement had a negative bias, and the analyte concentration and number of interferents has a moderately strong effect on the absolute error. The other studied factors did have a significant effect on the error; however, the PGM concentration does not have a significant quadratic component. It should be noted that the Cu-containing tests were excluded from the empirical model construction, because their high absolute error completely eclipsed the effect of all other parameters.

Ru 349.894 nm was similar to Rh 343.489 nm in that the model parameters did not explain a large proportion of the observed error variance (R^2 = 18%), and the magnitude of the significant factor parameters was small. These results suggest that the studied matrix parameters are not a major consideration for ruthenium quantification at 349.894 nm, as their effect on the absolute measurement error is small.

Os 225.585 nm was moderately affected by the matrix parameters (R^2 = 60%), as discussed above. The memory effects cause a strong positive measurement bias (β_0 = + 12.08 mg/L). PGM concentration had a strong non-linear impact on the error, which is consistent with a change in the relative importance of the memory effect contributions to the instrument response. The number of interferents and the concentration also had a strong impact.

Table S1. Summary of empirical model parameter coefficients. (*n.s.: not significant at α = 0.05)

Wavelengths	β_0	β_1	β_2	β_3	β_{23}	β_{11}	R^2
(nm)	(bias)	(PGM concentration)	(Number of interferents)	(Interferent concentration)	($X_2 \times X_3$)	(X_1^2)	(%)
Pt 214.423	-9.59	-2.27	-8.34	-2.43	-2.94	0.31	78
Pt 265.945	-2.48	-1.89	-0.67	-0.23	-0.42	0.67	71
Pt 299.797	-3.94	-1.73	-2.49	-0.84	-0.92	0.22	79
Pd 363.470	-5.61	-0.57	-3.50	-1.68	-1.33	1.61	23
Rh 233.477	-10.16	-3.10	-7.97	-2.19	-2.81	0.93	78
Rh 343.489	-1.44	0.13	-0.75	-0.68	-0.40	n.s.	15
Ir 224.268	-4.38	-2.24	-3.36	-0.78	-1.21	n.s.	82
Ru 349.894	-1.05	0.24	0.15	-0.59	n.s.	0.14	18
Os 225.585	12.08	-2.37	4.58	4.10	2.22	-3.31	60



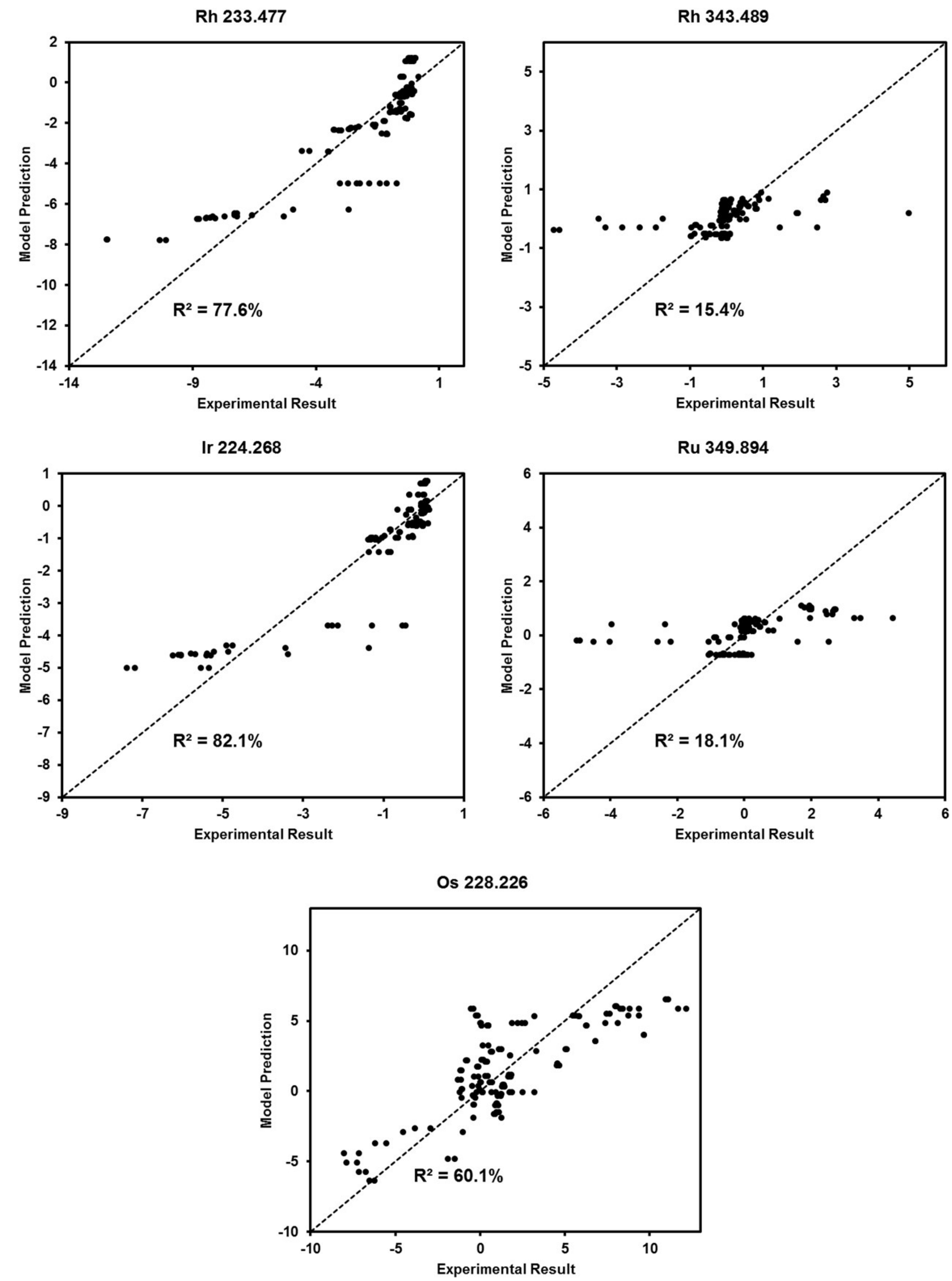


Figure S2. Correlation plots of the empirical absolute error models for each wavelength. The dashed line represents 100% correlation between the model prediction and the experimental result.

Table S2. Measurement relative standard deviation (%RSD) for each wavelength for all tested samples.

Sample ID		%RSD								
Sample Set	PGM Conc	Pt 214.423	Pt 265.945	Pt 299.797	Pd 363.470	Rh 233.477	Rh 343.489	Ir 224.268	Ru 349.894	Os 225.585
S1	0.1	37.021	45.549	17.857	3.221	17.488	8.589	14.598	44.415	2.305
S1	1	2.148	2.742	5.321	2.808	9.594	1.086	2.667	1.994	1.153
S1	5	0.957	0.641	0.934	1.223	1.019	0.902	0.505	1.220	0.425
S1	10	0.469	0.086	0.748	0.709	0.097	0.271	0.406	0.268	0.967
S1	50	0.698	0.714	0.658	0.655	0.762	0.566	0.801	0.544	1.115
S1	0.1	19.595	80.434	30.669	4.121	25.538	5.217	14.675	55.665	1.801
S1	1	2.636	3.389	3.500	3.002	3.505	0.559	2.740	3.199	1.113
S1	5	0.579	0.447	0.871	1.305	1.335	0.585	0.406	0.638	1.460
S1	10	0.681	0.162	0.538	0.441	0.617	0.242	0.511	0.462	0.802
S1	50	1.084	0.935	0.760	1.065	1.257	0.726	0.850	0.693	0.572
S2	0.1	22.890	23.995	30.165	151.096	20.695	5.777	10.227	24.874	26.956
S2	1	2.630	1.652	2.197	13.423	3.421	1.699	1.533	2.468	3.683
S2	5	0.583	0.500	0.567	1.437	0.839	1.155	0.717	1.550	1.848
S2	10	0.400	0.309	0.912	0.686	0.493	0.323	0.362	0.070	1.325
S2	50	0.670	0.585	0.566	0.632	0.681	0.603	0.581	0.604	1.187
S2	0.1	20.477	18.251	22.634	7.303	15.620	3.617	16.901	18.692	23.744
S2	1	1.221	1.829	6.230	43.932	2.771	0.436	1.548	2.912	1.783
S2	5	0.985	0.771	1.496	1.674	0.809	0.484	0.850	1.172	1.698
S2	10	5.622	5.298	5.081	7.220	5.896	4.375	5.564	4.247	1.173
S2	50	1.013	1.134	1.084	1.148	1.075	0.986	1.138	1.016	1.239
S3	0.1	5.784	25.448	48.312	16.007	54.679	6.201	7.086	15.150	22.615
S3	1	2.307	2.301	4.434	1260.04	2.727	0.813	1.057	2.207	2.042
S3	5	0.851	0.958	1.245	1.293	1.317	0.837	0.780	0.627	1.635
S3	10	0.840	0.692	0.290	1.296	0.637	0.548	0.422	0.788	0.518
S3	50	0.443	0.553	0.632	0.554	0.546	0.456	0.443	0.325	0.973
S3	0.1	10.236	13.641	179.841	4.955	46.724	2.837	8.032	15.567	18.513
S3	1	4.401	3.764	7.817	294.557	5.729	3.429	4.869	4.188	1.861
S3	5	0.570	0.221	0.478	0.816	1.105	0.251	0.442	0.543	1.833
S3	10	0.644	0.548	0.990	1.305	0.738	0.898	0.827	0.708	0.683
S3	50	0.630	0.626	0.477	0.581	0.727	0.456	0.489	0.459	1.204
S4A	0.1	78.187	100.369	36.338	7.397	203.677	12.669	7.208	17.953	3.007
S4A	1	0.313	5.093	4.236	8.430	3.160	0.940	1.508	3.291	1.005
S4A	5	4.343	3.983	4.948	3.523	5.742	1.432	3.838	1.378	2.039
S4A	10	0.279	0.276	0.868	0.660	0.562	0.290	0.378	0.214	0.923
S4A	50	0.622	0.570	0.328	0.787	0.813	0.507	0.727	0.371	0.587
S4A	0.1	275.734	232.835	27.959	104.248	66.464	7.438	11.275	29.848	4.551
S4A	1	2.075	0.926	5.493	15.061	2.265	0.955	1.795	2.847	1.230
S4A	5	3.526	3.788	3.941	1.183	4.111	2.189	4.212	2.673	2.342
S4A	10	0.602	0.538	0.783	0.949	0.702	0.364	0.651	0.228	1.037
S4A	50	5.948	5.411	5.050	5.753	6.539	4.655	5.342	4.500	2.709
S4B	0.1	29.073	30.896	64.701	3.193	30.792	7.880	14.057	39.064	2.814
S4B	1	4.915	4.001	6.531	2.813	4.913	0.856	3.405	3.819	1.256
S4B	5	1.043	0.805	0.747	2.734	0.946	0.624	0.459	0.914	1.371
S4B	10	0.444	0.510	0.548	1.044	0.558	0.436	0.352	0.588	0.944
S4B	50	0.475	0.362	0.321	0.570	0.524	0.426	0.566	0.367	1.014
S4B	0.1	20.477	18.251	22.634	7.303	15.620	3.617	16.901	18.692	23.744
S4B	1	1.221	1.829	6.230	43.932	2.771	0.436	1.548	2.912	1.783

Sample ID		%RSD								
Sample Set	PGM Conc	Pt 214.423	Pt 265.945	Pt 299.797	Pd 363.470	Rh 233.477	Rh 343.489	Ir 224.268	Ru 349.894	Os 225.585
S4B	5	0.985	0.771	1.496	1.674	0.809	0.484	0.850	1.172	1.698
S4B	10	5.622	5.298	5.081	7.220	5.896	4.375	5.564	4.247	1.173
S4B	50	1.013	1.134	1.084	1.148	1.075	0.986	1.138	1.016	1.239
S5	0.1	78.978	4.910	16.543	5.000	28.639	122.879	14.719	33.558	1.223
S5	1	3.592	7.831	1.799	3.143	2.390	0.773	2.299	2.532	0.727
S5	5	0.419	0.927	1.111	0.778	0.730	0.679	0.372	0.686	0.678
S5	10	0.331	0.339	0.304	0.364	0.429	0.303	0.341	0.353	0.384
S5	50	0.384	0.336	0.368	0.387	0.425	0.193	0.341	0.334	0.381
S5	0.1	60.157	10.701	11.423	2.971	34.436	65.665	6.624	44.311	0.932
S5	1	2.256	2.646	3.763	2.034	4.108	0.684	2.107	0.850	0.439
S5	5	1.190	0.733	0.604	0.525	0.741	0.467	1.195	0.493	0.577
S5	10	0.623	0.697	0.614	0.704	0.715	0.638	0.612	0.659	0.760
S5	50	3.247	3.016	2.918	3.139	3.512	2.882	2.948	2.812	3.107
S6	0.1	1.853	0.857	7.243	11.155	3.264	275.671	12.618	23.798	1.043
S6	1	39.430	1.794	1.703	11.482	9.814	1.528	2.692	1.978	0.727
S6	5	0.803	0.349	0.265	0.954	1.128	0.358	0.360	0.703	0.633
S6	10	0.265	0.252	0.104	0.389	0.228	0.239	0.283	0.229	0.389
S6	50	0.507	0.501	0.564	0.554	0.488	0.391	0.470	0.527	0.689
S6	0.1	2.216	1.411	6.873	1.628	4.220	2443.25	9.794	31.330	1.267
S6	1	17.456	0.826	1.427	1.762	6.518	1.009	1.596	1.270	1.297
S6	5	0.605	0.445	0.729	0.581	1.378	0.502	0.269	0.507	0.591
S6	10	0.437	0.264	0.414	0.310	0.722	0.287	0.244	0.251	0.377
S6	50	0.561	0.489	0.488	0.530	0.552	0.282	0.492	0.460	0.669
S7A	0.1	2.920	2.282	11.512	7.237	3.876	46.561	13.283	19.371	2.578
S7A	1	6.030	1.580	5.802	5.003	5.032	0.619	0.792	1.477	1.739
S7A	5	3.731	3.512	3.333	4.385	1.058	3.277	0.691	0.593	3.505
S7A	10	0.650	0.374	0.544	0.432	0.739	0.426	0.388	0.452	0.363
S7A	50	0.348	0.411	0.450	0.463	0.366	0.288	0.382	0.450	0.475
S7A	0.1	2.264	1.020	15.752	4.929	7.207	60.975	16.032	23.847	1.397
S7A	1	21.560	0.771	2.435	0.901	3.898	1.426	1.566	2.879	1.657
S7A	5	0.487	0.675	1.398	0.996	1.002	0.582	0.325	0.513	0.605
S7A	10	0.753	0.782	0.844	0.855	0.940	0.723	0.696	0.717	0.775
S7A	50	0.493	0.429	0.406	0.456	0.580	0.228	0.418	0.390	0.366
S7B	0.1	0.907	0.521	1.280	2.346	4.906	17.587	2.232	5.847	2.795
S7B	1	4.118	2.309	2.960	21.008	5.379	2.031	4.008	3.480	2.634
S7B	5	0.643	0.209	0.537	0.499	0.576	0.282	0.529	0.307	0.164
S7B	10	0.524	0.713	0.587	0.739	0.720	0.503	0.605	0.442	0.787
S7B	50	0.425	0.412	0.395	0.429	0.484	0.376	0.387	0.390	0.297
S7B	0.1	3.916	2.104	2.515	7.710	15.142	21.746	1.484	4.780	2.649
S7B	1	1.104	0.798	1.569	6.831	1.993	0.449	0.776	0.793	1.419
S7B	5	5.098	0.578	0.533	0.748	5.049	1.700	0.427	1.764	0.470
S7B	10	4.632	2.023	2.054	2.585	5.210	1.571	2.185	1.850	2.180
S7B	50	0.499	0.475	0.493	0.505	0.527	0.440	0.429	0.435	0.406
S8	0.1	3.818	2.179	10.797	4.373	13.625	33.322	4.006	13.322	1.140
S8	1	4.702	4.122	7.739	12.834	4.728	2.913	4.145	1.072	5.768
S8	5	0.441	0.373	0.910	1.023	0.884	0.274	0.972	0.308	0.297
S8	10	0.382	0.390	0.415	0.467	0.517	0.454	0.427	0.425	0.419
S8	50	0.638	0.608	0.619	0.628	0.676	0.577	0.578	0.559	0.672
S8	0.1	4.240	1.394	7.839	3.934	4.945	27.012	8.005	26.337	4.345
S8	1	5.100	4.759	4.420	13.953	4.245	3.273	3.909	4.047	4.748

Sample ID		%RSD								
Sample Set	PGM Conc	Pt 214.423	Pt 265.945	Pt 299.797	Pd 363.470	Rh 233.477	Rh 343.489	Ir 224.268	Ru 349.894	Os 225.585
S8	5	0.855	3.526	1.193	4.651	0.725	3.224	0.401	3.142	3.721
S8	10	0.659	0.242	0.566	0.309	0.800	0.283	0.277	0.205	0.376
S8	50	0.231	0.231	0.233	0.228	0.276	0.123	0.200	0.233	0.159
S9	0.1	10.717	2.333	9.915	5.661	10.812	13.752	13.879	24.054	2.367
S9	1	5.288	0.951	4.769	4.596	0.749	1.513	1.678	1.905	0.410
S9	5	1.022	0.303	0.723	1.873	1.078	0.193	1.431	0.235	0.422
S9	10	0.609	0.633	0.549	0.731	0.680	0.664	0.598	0.640	0.603
S9	50	0.560	0.477	0.461	0.520	0.575	0.250	0.495	0.450	0.455
S9	0.1	9.263	1.565	20.372	4.104	9.776	7.191	20.435	19.769	1.805
S9	1	5.486	1.361	4.757	4.755	2.652	1.178	2.219	2.033	2.102
S9	5	0.884	0.313	0.661	0.553	0.678	0.268	0.581	0.250	0.206
S9	10	0.474	0.383	0.512	0.445	0.608	0.433	0.440	0.385	0.489
S9	50	0.413	0.402	0.416	0.449	0.403	0.415	0.399	0.413	0.442
S10A	0.1	7.537	1.793	17.087	4.866	4.551	16.575	6.166	38.552	2.369
S10A	1	5.246	3.635	5.012	15.437	3.390	2.955	2.458	3.852	4.762
S10A	5	0.297	0.398	0.790	0.354	0.628	0.452	1.260	0.482	0.396
S10A	10	0.713	0.676	0.540	0.759	0.881	0.573	0.620	0.581	0.661
S10A	50	0.554	0.457	0.490	0.516	0.612	0.259	0.491	0.432	0.558
S10A	0.1	3.739	2.117	12.278	1.887	8.246	23.557	10.985	16.110	2.342
S10A	1	2.951	2.877	4.462	13.713	5.483	2.627	4.875	2.714	4.261
S10A	5	0.833	0.450	1.199	0.505	1.079	0.260	0.467	0.191	0.195
S10A	10	2.731	2.515	2.500	2.906	2.961	2.193	2.515	2.313	2.676
S10A	50	0.305	0.264	0.252	0.307	0.294	0.255	0.276	0.267	0.434
S10B	0.1	0.751	1.199	1.594	4.691	25.480	4.156	0.683	3.340	2.638
S10B	1	18.347	1.686	1.653	5.804	2.332	0.906	1.378	1.587	1.437
S10B	5	0.496	0.734	0.760	0.863	0.674	0.336	0.506	0.335	0.531
S10B	10	0.330	0.559	0.267	0.600	0.308	0.417	0.550	0.516	0.613
S10B	50	0.492	0.460	0.459	0.469	0.510	0.396	0.445	0.403	0.443
S10B	0.1	0.476	0.459	3.307	4.948	41.489	4.287	1.217	3.333	4.975
S10B	1	10.434	0.295	0.712	2.386	1.826	0.411	0.563	0.939	0.783
S10B	5	3.938	2.593	2.769	3.206	0.755	0.413	3.576	0.415	2.324
S10B	10	0.617	0.444	0.667	0.415	0.543	0.281	0.372	0.334	0.406
S10B	50	0.448	0.421	0.434	0.431	0.501	0.375	0.402	0.369	0.465
S12	0.1	2.436	5.288	5.533	33.918	3.377	1.953	0.658	2.337	1.202
S12	1	0.423	0.720	1.025	0.715	0.737	0.435	0.792	0.321	0.413
S12	5	0.475	0.343	0.450	0.250	0.475	0.558	0.829	0.221	0.191
S12	10	0.506	0.378	0.304	0.322	0.415	0.291	0.332	0.300	0.333
S12	50	0.353	0.306	0.280	0.337	0.393	0.292	0.416	0.256	0.316
S12	0.1	2.080	2.411	5.451	30.403	1.812	1.291	0.183	2.046	1.144
S12	1	0.979	0.181	0.553	2.031	0.564	0.173	0.533	0.503	0.419
S12	5	0.459	0.159	0.359	0.952	0.486	0.666	0.287	0.637	0.770
S12	10	0.612	0.651	0.692	0.505	0.748	0.362	0.470	0.310	0.367
S12	50	0.459	0.471	0.470	0.461	0.584	0.440	0.542	0.418	0.463

Table S3. Experimental calculation matrix (X) for all tested samples (refer to Table 4 for factor level coding).

Sample ID		Calculation Matrix					
Sample Set	PGM Conc.	X_0	X_1	X_2	X_3	$X_2 \times X_3$	X_1^2
S1	0.1	1	-1	-1	-1	1	1
S1	1	1	-0.96	-1	-1	1	0.93
S1	5	1	-0.8	-1	-1	1	0.65
S1	10	1	-0.6	-1	-1	1	0.36
S1	50	1	1	-1	-1	1	1
S1	0.1	1	-1	-1	-1	1	1
S1	1	1	-0.96	-1	-1	1	0.93
S1	5	1	-0.8	-1	-1	1	0.65
S1	10	1	-0.6	-1	-1	1	0.36
S1	50	1	1	-1	-1	1	1
S2	0.1	1	-1	-1	-1	1	1
S2	1	1	-0.96	-1	-1	1	0.93
S2	5	1	-0.8	-1	-1	1	0.65
S2	10	1	-0.6	-1	-1	1	0.36
S2	50	1	1	-1	-1	1	1
S2	0.1	1	-1	-1	-1	1	1
S2	1	1	-0.96	-1	-1	1	0.93
S2	5	1	-0.8	-1	-1	1	0.65
S2	10	1	-0.6	-1	-1	1	0.36
S2	50	1	1	-1	-1	1	1
S3	0.1	1	-1	-1	-1	1	1
S3	1	1	-0.96	-1	-1	1	0.93
S3	5	1	-0.8	-1	-1	1	0.65
S3	10	1	-0.6	-1	-1	1	0.36
S3	50	1	1	-1	-1	1	1
S3	0.1	1	-1	-1	-1	1	1
S3	1	1	-0.96	-1	-1	1	0.93
S3	5	1	-0.8	-1	-1	1	0.65
S3	10	1	-0.6	-1	-1	1	0.36
S3	50	1	1	-1	-1	1	1
S4A	0.1	1	-1	-0.71	-1	0.71	1
S4A	1	1	-0.96	-0.71	-2	1.43	0.93
S4A	5	1	-0.8	-0.71	-2	1.43	0.65
S4A	10	1	-0.6	-0.71	-2	1.43	0.36
S4A	50	1	1	-0.71	-2	1.43	1
S4A	0.1	1	-1	-0.71	-2	1.43	1
S4A	1	1	-0.96	-0.71	-2	1.43	0.93
S4A	5	1	-0.8	-0.71	-2	1.43	0.65
S4A	10	1	-0.6	-0.71	-2	1.43	0.36
S4A	50	1	1	-0.71	-2	1.43	1
S4B	0.1	1	-1	-0.71	-1	0.71	1
S4B	1	1	-0.96	-0.71	-1	0.71	0.93
S4B	5	1	-0.8	-0.71	-1	0.71	0.65
S4B	10	1	-0.6	-0.71	-1	0.71	0.36
S4B	50	1	1	-0.71	-1	0.71	1
S4B	0.1	1	-1	-0.71	-1	0.71	1
S4B	1	1	-0.96	-0.71	-1	0.71	0.93

Sample ID		Calculation Matrix					
Sample Set	PGM Conc.	X_0	X_1	X_2	X_3	$X_2 \times X_3$	X_1^2
S4B	5	1	-0.8	-0.71	-1	0.71	0.65
S4B	10	1	-0.6	-0.71	-1	0.71	0.36
S4B	50	1	1	-0.71	-1	0.71	1
S5	0.1	1	-1	-0.43	-2.33	1	1
S5	1	1	-0.96	-0.43	-2.33	1	0.93
S5	5	1	-0.8	-0.43	-2.33	1	0.65
S5	10	1	-0.6	-0.43	-2.33	1	0.36
S5	50	1	1	-0.43	-2.33	1	1
S5	0.1	1	-1	-0.43	-2.33	1	1
S5	1	1	-0.96	-0.43	-2.33	1	0.93
S5	5	1	-0.8	-0.43	-2.33	1	0.65
S5	10	1	-0.6	-0.43	-2.33	1	0.36
S5	50	1	1	-0.43	-2.33	1	1
S6	0.1	1	-1	-0.14	-2.5	0.36	1
S6	1	1	-0.96	-0.14	-2.5	0.36	0.93
S6	5	1	-0.8	-0.14	-2.5	0.36	0.65
S6	10	1	-0.6	-0.14	-2.5	0.36	0.36
S6	50	1	1	-0.14	-2.5	0.36	1
S6	0.1	1	-1	-0.14	-2.5	0.36	1
S6	1	1	-0.96	-0.14	-2.5	0.36	0.93
S6	5	1	-0.8	-0.14	-2.5	0.36	0.65
S6	10	1	-0.6	-0.14	-2.5	0.36	0.36
S6	50	1	1	-0.14	-2.5	0.36	1
S7A	0.1	1	-1	0.14	-2.6	-0.37	1
S7A	1	1	-0.96	0.14	-2.6	-0.37	0.93
S7A	5	1	-0.8	0.14	-2.6	-0.37	0.65
S7A	10	1	-0.6	0.14	-2.6	-0.37	0.36
S7A	50	1	1	0.14	-2.6	-0.37	1
S7A	0.1	1	-1	0.14	-2.6	-0.37	1
S7A	1	1	-0.96	0.14	-2.6	-0.37	0.93
S7A	5	1	-0.8	0.14	-2.6	-0.37	0.65
S7A	10	1	-0.6	0.14	-2.6	-0.37	0.36
S7A	50	1	1	0.14	-2.6	-0.37	1
S7B	0.1	1	-1	0.14	-2.2	-0.31	1
S7B	1	1	-0.96	0.14	-2.2	-0.31	0.93
S7B	5	1	-0.8	0.14	-2.2	-0.31	0.65
S7B	10	1	-0.6	0.14	-2.2	-0.31	0.36
S7B	50	1	1	0.14	-2.2	-0.31	1
S7B	0.1	1	-1	0.14	-2.2	-0.31	1
S7B	1	1	-0.96	0.14	-2.2	-0.31	0.93
S7B	5	1	-0.8	0.14	-2.2	-0.31	0.65
S7B	10	1	-0.6	0.14	-2.2	-0.31	0.36
S7B	50	1	1	0.14	-2.2	-0.31	1
S8	0.1	1	-1	0.43	-2.67	-1.14	1
S8	1	1	-0.96	0.43	-2.67	-1.14	0.93
S8	5	1	-0.8	0.43	-2.67	-1.14	0.65
S8	10	1	-0.6	0.43	-2.67	-1.14	0.36
S8	50	1	1	0.43	-2.67	-1.14	1
S8	0.1	1	-1	0.43	-2.67	-1.14	1
S8	1	1	-0.96	0.43	-2.67	-1.14	0.93

Sample ID		Calculation Matrix					
Sample Set	PGM Conc.	X_0	X_1	X_2	X_3	$X_2 \times X_3$	X_1^2
S8	5	1	-0.8	0.43	-2.67	-1.14	0.65
S8	10	1	-0.6	0.43	-2.67	-1.14	0.36
S8	50	1	1	0.43	-2.67	-1.14	1
S9	0.1	1	-1	0.71	-2.71	-1.94	1
S9	1	1	-0.96	0.71	-2.71	-1.94	0.93
S9	5	1	-0.8	0.71	-2.71	-1.94	0.65
S9	10	1	-0.6	0.71	-2.71	-1.94	0.36
S9	50	1	1	0.71	-2.71	-1.94	1
S9	0.1	1	-1	0.71	-2.71	-1.94	1
S9	1	1	-0.96	0.71	-2.71	-1.94	0.93
S9	5	1	-0.8	0.71	-2.71	-1.94	0.65
S9	10	1	-0.6	0.71	-2.71	-1.94	0.36
S9	50	1	1	0.71	-2.71	-1.94	1
S10A	0.1	1	-1	1	-2.75	-2.75	1
S10A	1	1	-0.96	1	-2.75	-2.75	0.93
S10A	5	1	-0.8	1	-2.75	-2.75	0.65
S10A	10	1	-0.6	1	-2.75	-2.75	0.36
S10A	50	1	1	1	-2.75	-2.75	1
S10A	0.1	1	-1	1	-2.75	-2.75	1
S10A	1	1	-0.96	1	-2.75	-2.75	0.93
S10A	5	1	-0.8	1	-2.75	-2.75	0.65
S10A	10	1	-0.6	1	-2.75	-2.75	0.36
S10A	50	1	1	1	-2.75	-2.75	1
S10B	0.1	1	-1	1	-2.5	-2.5	1
S10B	1	1	-0.96	1	-2.5	-2.5	0.93
S10B	5	1	-0.8	1	-2.5	-2.5	0.65
S10B	10	1	-0.6	1	-2.5	-2.5	0.36
S10B	50	1	1	1	-2.5	-2.5	1
S10B	0.1	1	-1	1	-2.5	-2.5	1
S10B	1	1	-0.96	1	-2.5	-2.5	0.93
S10B	5	1	-0.8	1	-2.5	-2.5	0.65
S10B	10	1	-0.6	1	-2.5	-2.5	0.36
S10B	50	1	1	1	-2.5	-2.5	1
S12	0.1	1	-1	-1	-1	1	1
S12	1	1	-0.96	-1	-1	1	0.93
S12	5	1	-0.8	-1	-1	1	0.65
S12	10	1	-0.6	-1	-1	1	0.36
S12	50	1	1	-1	-1	1	1
S12	0.1	1	-1	-1	-1	1	1
S12	1	1	-0.96	-1	-1	1	0.93
S12	5	1	-0.8	-1	-1	1	0.65
S12	10	1	-0.6	-1	-1	1	0.36
S12	50	1	1	-1	-1	1	1

Table S4. Measured absolute error response matrix (Y) for each wavelength for the all the tested samples.

Sample ID		Response Matrices ($Y_{element}$)								
Sample Set	**PGM Conc**	**Pt 214.423**	**Pt 265.945**	**Pt 299.797**	**Pd 363.470**	**Rh 233.477**	**Rh 343.489**	**Ir 224.268**	**Ru 349.894**	**Os 225.585**
S1	0.1	-0.179	-0.154	0.011	3.710	-0.254	0.040	0.083	-0.052	6.247
S1	1	-0.250	-0.209	-0.080	3.631	-0.325	-0.006	0.034	-0.077	7.389
S1	5	-0.627	-0.437	-0.470	-0.240	-0.514	-0.267	-0.135	-0.282	9.377
S1	10	-1.052	-0.619	-0.487	0.205	-0.771	-0.472	-0.312	-0.644	11.674
S1	50	-2.997	-2.422	-2.386	-1.209	-3.038	-2.377	-2.280	-2.591	2.507
S1	0.1	-0.172	-0.158	0.017	2.804	-0.187	0.033	0.060	-0.071	6.297
S1	1	-0.290	-0.301	-0.145	2.622	-0.376	-0.060	-0.022	-0.126	8.109
S1	5	-0.826	-0.459	-0.329	-0.257	-0.540	-0.309	-0.128	-0.481	8.757
S1	10	-1.097	-0.635	-0.613	-0.273	-0.777	-0.575	-0.312	-0.732	12.136
S1	50	-2.249	-1.656	-1.975	-1.054	-2.342	-1.942	-1.286	-2.197	3.184
S2	0.1	-0.009	0.025	0.054	-0.188	-0.004	0.019	0.049	0.020	0.419
S2	1	-0.083	-0.072	-0.065	-0.160	-0.111	-0.063	-0.035	-0.047	1.861
S2	5	-0.341	-0.321	-0.396	-0.066	-0.462	-0.455	-0.353	-0.438	5.579
S2	10	-0.555	-0.638	-0.720	-0.878	-0.760	-0.882	-0.660	-1.067	8.813
S2	50	-1.604	-2.003	-2.199	-1.767	-2.209	-2.861	-2.145	-4.026	1.882
S2	0.1	-0.008	-0.031	-0.020	-0.845	0.002	0.005	0.036	0.005	0.486
S2	1	-0.133	-0.164	-0.118	-0.900	-0.135	-0.120	-0.078	-0.090	2.454
S2	5	-0.372	-0.337	-0.391	-1.040	-0.521	-0.506	-0.361	-0.611	5.485
S2	10	-0.307	-0.386	-0.536	-0.760	-0.494	-0.622	-0.369	-0.844	9.376
S2	50	-2.216	-2.298	-2.710	-2.704	-2.695	-3.318	-2.380	-4.502	1.730
S3	0.1	0.145	0.003	-0.037	-0.771	-0.121	0.029	0.088	0.036	0.478
S3	1	0.039	-0.094	-0.129	-1.008	-0.205	-0.043	-0.026	-0.015	2.214
S3	5	0.058	0.013	-0.161	-0.775	-0.555	-0.125	0.014	-0.141	5.613
S3	10	0.158	-0.023	-0.163	-0.711	-0.464	-0.079	0.050	-0.105	8.252
S3	50	-0.420	-0.432	-0.602	-1.480	-1.125	-0.732	-0.527	-0.773	0.677
S3	0.1	0.132	0.006	-0.065	-1.462	-0.113	0.017	0.046	-0.006	0.491
S3	1	0.126	-0.059	-0.118	-0.881	-0.175	-0.008	0.042	0.003	2.633
S3	5	0.022	0.015	-0.129	-1.223	-0.588	-0.110	-0.021	-0.142	5.461
S3	10	0.067	-0.009	-0.245	-1.204	-0.537	-0.125	0.077	-0.175	8.419
S3	50	-0.694	-0.496	-0.883	-2.082	-1.411	-0.967	-0.447	-1.072	0.907
S4A	0.1	-0.073	-0.084	0.006	0.469	-0.114	0.006	0.047	-0.020	3.213
S4A	1	-0.232	-0.217	-0.106	0.321	-0.284	-0.122	-0.062	-0.104	5.021
S4A	5	-0.659	-0.319	-0.317	0.519	-0.594	-0.433	-0.188	-0.481	6.791
S4A	10	-1.140	-0.831	-0.876	-1.430	-1.199	-0.819	-0.599	-0.845	9.647
S4A	50	-3.921	-3.349	-3.572	-4.164	-4.915	-3.505	-3.439	-3.964	-0.399
S4A	0.1	-0.094	-0.094	-0.033	-0.145	-0.128	0.013	0.049	-0.008	3.296
S4A	1	-0.230	-0.260	-0.179	-0.244	-0.333	-0.133	-0.063	-0.106	5.114
S4A	5	-0.642	-0.309	-0.324	-0.019	-0.523	-0.383	-0.185	-0.412	6.804
S4A	10	-1.251	-0.836	-0.958	-1.662	-1.253	-0.867	-0.606	-0.902	9.670
S4A	50	-2.167	-1.145	-1.637	-2.281	-2.664	-1.745	-1.371	-2.373	1.253
S4B	0.1	-0.164	-0.149	0.000	2.628	-0.222	0.012	0.084	-0.032	5.836
S4B	1	-0.342	-0.313	-0.151	2.323	-0.409	-0.130	-0.060	-0.165	7.465
S4B	5	-1.100	-0.695	-0.636	-0.865	-0.998	-0.578	-0.440	-0.648	8.057
S4B	10	-1.654	-1.155	-1.100	-0.894	-1.587	-0.966	-0.818	-1.003	11.079
S4B	50	-6.017	-4.941	-4.899	-5.568	-7.298	-4.720	-4.914	-5.011	-0.012
S4B	0.1	-0.174	-0.164	-0.028	1.964	-0.232	0.019	0.063	-0.050	5.815
S4B	1	-0.361	-0.324	-0.199	1.817	-0.474	-0.138	-0.056	-0.157	7.640

Sample ID		Response Matrices ($Y_{element}$)								
Sample Set	**PGM Conc**	**Pt 214.423**	**Pt 265.945**	**Pt 299.797**	**Pd 363.470**	**Rh 233.477**	**Rh 343.489**	**Ir 224.268**	**Ru 349.894**	**Os 225.585**
S4B	5	-1.074	-0.672	-0.581	-0.959	-0.987	-0.566	-0.434	-0.605	7.955
S4B	10	-1.760	-1.158	-1.147	-1.376	-1.687	-0.986	-0.844	-1.037	10.930
S4B	50	-6.125	-4.591	-4.819	-5.775	-7.199	-4.582	-4.752	-4.917	0.025
S5	0.1	-0.068	-0.391	0.297	1.063	-0.031	-0.107	0.051	-0.042	4.651
S5	1	-0.149	-0.447	0.221	0.955	-0.124	-0.193	-0.054	-0.078	4.544
S5	5	-0.621	-0.823	-0.206	0.049	-0.594	-0.078	-0.381	0.108	1.755
S5	10	-1.628	-1.968	-0.958	-0.015	-2.567	0.021	-1.313	0.233	1.092
S5	50	-5.733	-5.183	-4.021	0.542	-7.698	0.431	-5.690	1.960	-4.537
S5	0.1	-0.069	-0.292	0.250	1.441	-0.031	-0.118	0.044	-0.013	4.505
S5	1	-0.164	-0.336	0.187	1.357	-0.101	-0.183	-0.029	-0.078	4.539
S5	5	-0.637	-0.679	-0.165	-0.022	-0.505	-0.112	-0.301	0.075	1.772
S5	10	-1.600	-1.955	-0.944	0.000	-2.575	0.071	-1.272	0.274	1.255
S5	50	-3.222	-3.017	-1.727	3.527	-5.307	4.974	-3.385	4.427	-1.013
S6	0.1	-0.993	1.655	0.465	0.479	-0.566	-0.097	0.033	0.003	1.800
S6	1	-1.093	1.635	0.406	0.460	-0.639	-0.151	-0.027	-0.016	1.835
S6	5	-1.463	0.412	-0.080	-0.189	-0.983	0.103	-0.252	-0.129	-0.101
S6	10	-2.266	-0.133	-0.609	-0.250	-3.251	0.282	-1.162	0.470	-0.838
S6	50	-6.453	-3.543	-3.890	0.749	-8.098	0.791	-5.305	2.625	-6.207
S6	0.1	-1.002	1.763	0.490	1.103	-0.515	-0.101	0.043	0.012	1.666
S6	1	-1.099	1.712	0.466	1.139	-0.555	-0.157	-0.033	0.001	1.677
S6	5	-1.457	0.282	0.144	-0.406	-0.833	-0.010	-0.271	0.142	-0.175
S6	10	-2.319	-0.200	-0.620	-0.348	-3.282	0.265	-1.206	0.457	-0.766
S6	50	-6.696	-3.729	-4.042	0.605	-8.468	0.825	-5.415	2.459	-5.533
S7A	0.1	-0.717	1.537	0.381	0.304	-0.476	-0.081	0.029	0.000	1.442
S7A	1	-0.832	1.455	0.281	0.168	-0.557	-0.147	-0.061	-0.060	1.381
S7A	5	-1.226	0.482	-0.008	-0.074	-1.010	0.294	-0.393	-0.294	-0.095
S7A	10	-2.166	-0.379	-0.791	-0.619	-2.968	0.237	-1.322	0.405	-1.165
S7A	50	-7.267	-4.506	-4.780	-0.774	-8.745	0.528	-6.236	2.422	-8.050
S7A	0.1	-0.723	1.565	0.402	1.193	-0.361	-0.077	0.027	0.001	1.272
S7A	1	-0.826	1.515	0.332	1.134	-0.439	-0.154	-0.041	-0.065	1.314
S7A	5	-1.220	0.116	-0.032	-0.519	-0.741	-0.010	-0.291	0.121	-0.359
S7A	10	-2.263	-0.462	-0.888	-0.736	-3.071	0.189	-1.387	0.352	-1.114
S7A	50	-7.187	-4.344	-4.594	-0.544	-8.824	0.768	-6.047	2.649	-7.154
S7B	0.1	-1.455	2.234	0.519	-0.608	-0.210	-0.091	-0.015	-0.024	0.401
S7B	1	-1.643	2.164	0.422	-0.640	-0.384	-0.077	-0.170	0.013	0.170
S7B	5	-2.388	0.797	-0.068	-0.844	-1.343	-0.082	-0.704	0.108	0.614
S7B	10	-3.322	0.238	-0.647	-0.863	-4.561	0.366	-1.362	0.713	0.154
S7B	50	-10.078	-4.848	-5.498	-0.843	-12.479	1.922	-7.396	3.468	-3.847
S7B	0.1	-1.492	2.301	0.545	-0.579	-0.175	-0.093	-0.011	-0.021	0.314
S7B	1	-1.618	2.118	0.410	-0.696	-0.372	-0.095	-0.189	-0.004	0.083
S7B	5	-2.256	0.844	-0.046	-0.687	-1.134	0.036	-0.642	0.230	0.698
S7B	10	-3.076	0.478	-0.452	-0.573	-4.257	0.529	-1.120	0.860	0.495
S7B	50	-10.245	-4.791	-5.562	-0.823	-12.471	1.943	-7.187	3.272	-2.945
S8	0.1	-0.615	1.273	0.385	0.544	-0.376	-0.067	0.035	0.037	1.200
S8	1	-0.668	1.291	0.326	0.761	-0.472	-0.129	-0.009	-0.070	1.227
S8	5	-1.061	0.107	-0.052	0.150	-0.855	0.055	-0.294	0.036	-0.471
S8	10	-1.920	-0.375	-0.669	-0.368	-2.671	0.346	-1.280	0.190	-1.301
S8	50	-6.752	-4.351	-4.342	0.619	-8.279	2.702	-6.110	1.949	-7.882
S8	0.1	-0.590	1.335	0.352	1.431	-0.286	-0.072	0.013	0.003	1.027
S8	1	-0.664	1.458	0.331	1.864	-0.327	-0.110	0.006	-0.022	1.234

Sample ID		Response Matrices ($Y_{element}$)								
Sample Set	**PGM Conc**	**Pt 214.423**	**Pt 265.945**	**Pt 299.797**	**Pd 363.470**	**Rh 233.477**	**Rh 343.489**	**Ir 224.268**	**Ru 349.894**	**Os 225.585**
S8	5	-0.984	0.429	0.016	0.053	-0.546	0.367	-0.214	0.340	-0.100
S8	10	-1.917	-0.344	-0.660	-0.310	-2.645	0.387	-1.233	0.217	-1.119
S8	50	-6.802	-4.160	-4.321	0.489	-8.435	0.895	-6.047	2.003	-7.261
S9	0.1	-0.474	1.109	0.248	0.706	-0.332	-0.055	0.026	0.003	1.050
S9	1	-0.582	1.047	0.235	0.566	-0.423	-0.131	-0.041	-0.083	1.001
S9	5	-0.978	0.079	-0.095	0.041	-0.763	0.101	-0.281	0.107	-0.422
S9	10	-1.613	-0.260	-0.596	0.025	-2.388	0.504	-1.038	0.417	-1.047
S9	50	-5.666	-3.279	-3.472	1.215	-7.212	0.862	-5.399	1.992	-7.171
S9	0.1	-0.480	1.142	0.277	1.199	-0.247	-0.047	0.021	0.004	0.883
S9	1	-0.578	1.093	0.206	0.925	-0.316	-0.131	-0.031	-0.045	0.966
S9	5	-0.924	0.062	-0.084	-0.255	-0.568	0.092	-0.248	0.097	-0.380
S9	10	-1.830	-0.424	-0.715	-0.230	-2.605	0.388	-1.188	0.310	-1.095
S9	50	-6.284	-3.878	-3.723	1.032	-8.177	2.646	-5.796	1.789	-6.762
S10A	0.1	-0.445	0.994	0.260	0.808	-0.296	-0.045	0.112	-0.013	0.901
S10A	1	-0.464	1.151	0.312	1.459	-0.284	-0.064	0.139	0.034	1.087
S10A	5	-0.837	0.074	-0.049	0.161	-0.597	0.120	-0.134	0.138	-0.411
S10A	10	-1.516	-0.303	-0.598	-0.141	-2.274	0.427	-0.974	0.322	-1.098
S10A	50	-5.098	-2.954	-3.130	1.340	-6.594	0.946	-4.860	1.949	-6.524
S10A	0.1	-0.428	1.005	0.239	0.984	-0.197	-0.050	0.075	0.019	0.800
S10A	1	-0.492	1.037	0.280	1.329	-0.218	-0.095	0.079	0.000	0.942
S10A	5	-0.749	0.046	0.027	-0.307	-0.384	0.117	-0.085	0.133	-0.377
S10A	10	-0.847	0.435	0.106	0.669	-1.606	1.156	-0.289	1.059	-0.278
S10A	50	-5.589	-3.480	-3.401	1.245	-7.308	2.745	-5.224	1.704	-6.219
S10B	0.1	-0.908	1.468	0.331	-0.485	-0.136	-0.057	0.109	-0.012	0.154
S10B	1	-1.049	1.397	0.249	-0.486	-0.305	-0.043	-0.021	0.028	-0.018
S10B	5	-1.666	0.450	-0.110	-0.506	-1.104	0.035	-0.374	0.110	0.556
S10B	10	-2.393	0.093	-0.482	-0.340	-3.514	0.580	-0.886	0.600	0.297
S10B	50	-8.029	-3.418	-3.895	1.529	-10.324	2.578	-5.542	2.695	-1.917
S10B	0.1	-0.915	1.493	0.342	-0.471	-0.115	-0.057	0.110	-0.008	0.122
S10B	1	-1.048	1.369	0.228	-0.537	-0.300	-0.054	-0.038	0.009	-0.042
S10B	5	-1.631	0.562	-0.056	-0.349	-1.167	0.026	-0.261	0.104	0.703
S10B	10	-2.389	0.148	-0.473	-0.289	-3.488	0.605	-0.830	0.629	0.438
S10B	50	-7.883	-3.299	-3.798	1.669	-10.076	2.701	-5.344	2.719	-1.511
S12	0.1	-0.205	0.015	0.031	-0.033	0.019	0.024	609.456	0.027	0.069
S12	1	-0.270	-0.039	-0.032	-0.152	-0.090	0.014	609.558	0.026	-0.015
S12	5	-0.533	-0.219	-0.246	-0.107	-0.478	0.010	576.848	0.047	-0.251
S12	10	-0.836	-0.331	-0.359	-0.245	-0.671	-0.049	580.231	0.088	-0.552
S12	50	-1.389	-0.816	-1.001	0.584	-1.852	1.451	583.803	1.585	-1.223
S12	0.1	-0.201	0.022	0.044	-0.013	0.022	0.030	625.799	0.034	0.085
S12	1	-0.239	-0.002	-0.007	-0.060	-0.057	0.042	619.113	0.045	0.022
S12	5	-0.120	-0.169	-0.192	-0.022	0.162	0.090	614.576	0.095	-0.146
S12	10	-0.665	-0.133	-0.243	-0.061	-0.508	0.088	596.327	0.208	-0.397
S12	50	-0.245	0.209	-0.076	1.617	-0.720	2.474	597.770	2.520	-0.207