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Statistical Modeling of ICP-OES Interferences for Platinum Analysis

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International Precious Metals Institute
Sampling and Analytical Committee
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Outline

Inductively Coupled Plasma - Optical Emission Spectroscopy
- Operation and matrix effects

Statistical Modeling
- Why and How

Application of a Statistical Model
- Design and validation

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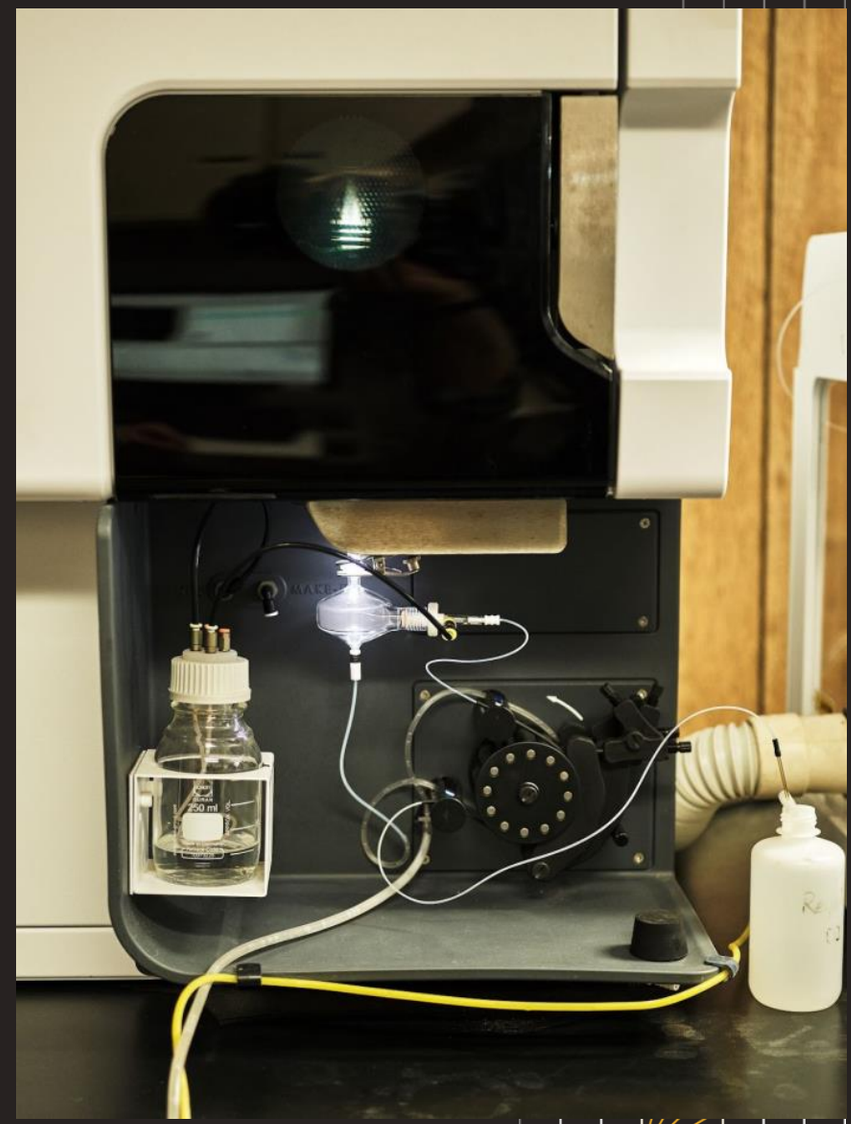
ICP-OES

Inductively-Coupled Plasma

Optical Emission Spectroscopy

Analyzes the elemental composition of a solution sample



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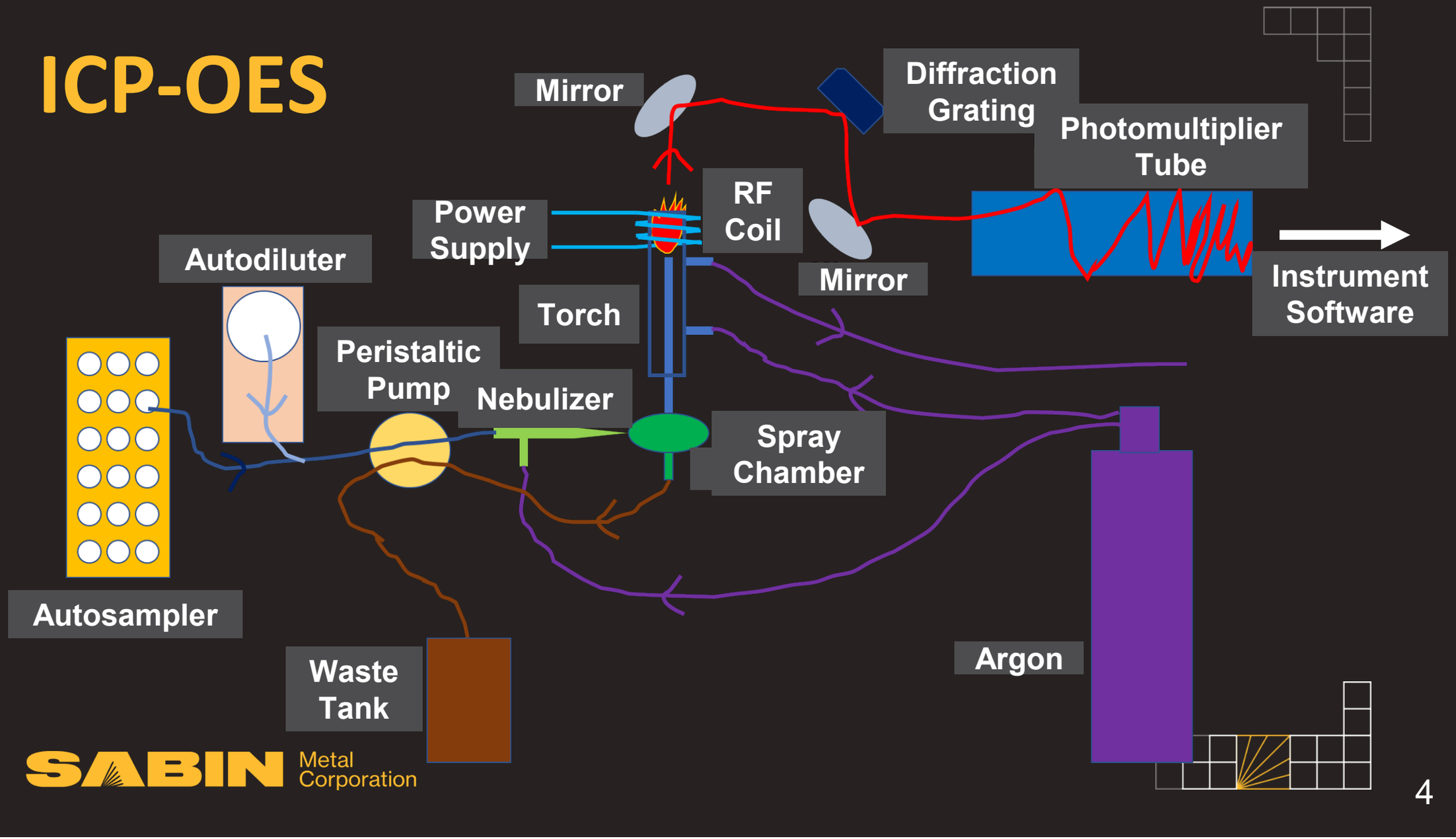

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Solution Sample

Contains analyte and other components

Other components make up the solution matrix
    Water, acids, organics, dissolved solids

The matrix affects the measurement of the analyte

How can we reduce matrix effects before analyzing?

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Solution Sample

How can we reduce matrix effects before analyzing?

- Separate the analyte from the matrix
- Match standards to the sample matrix
- Standard addition

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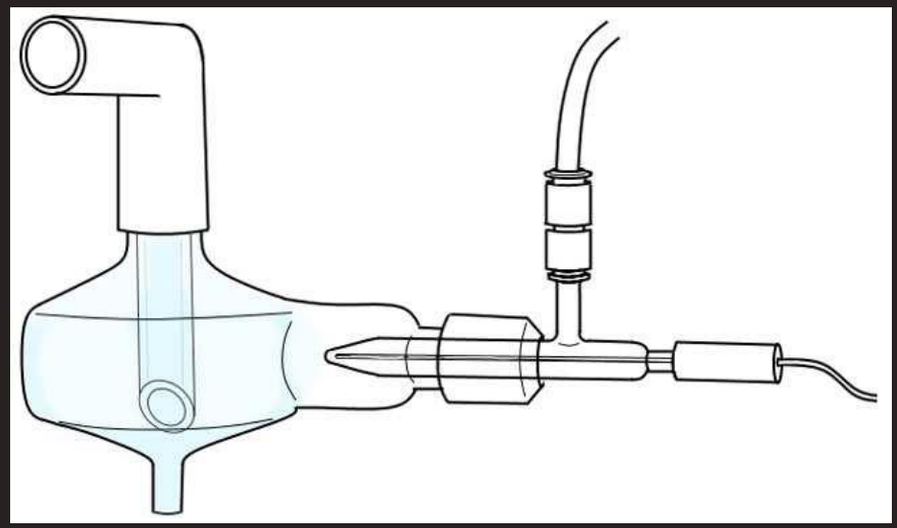
Nebulizer and Spray Chamber

Aerosolizes sample

Aerosol is carried to torch



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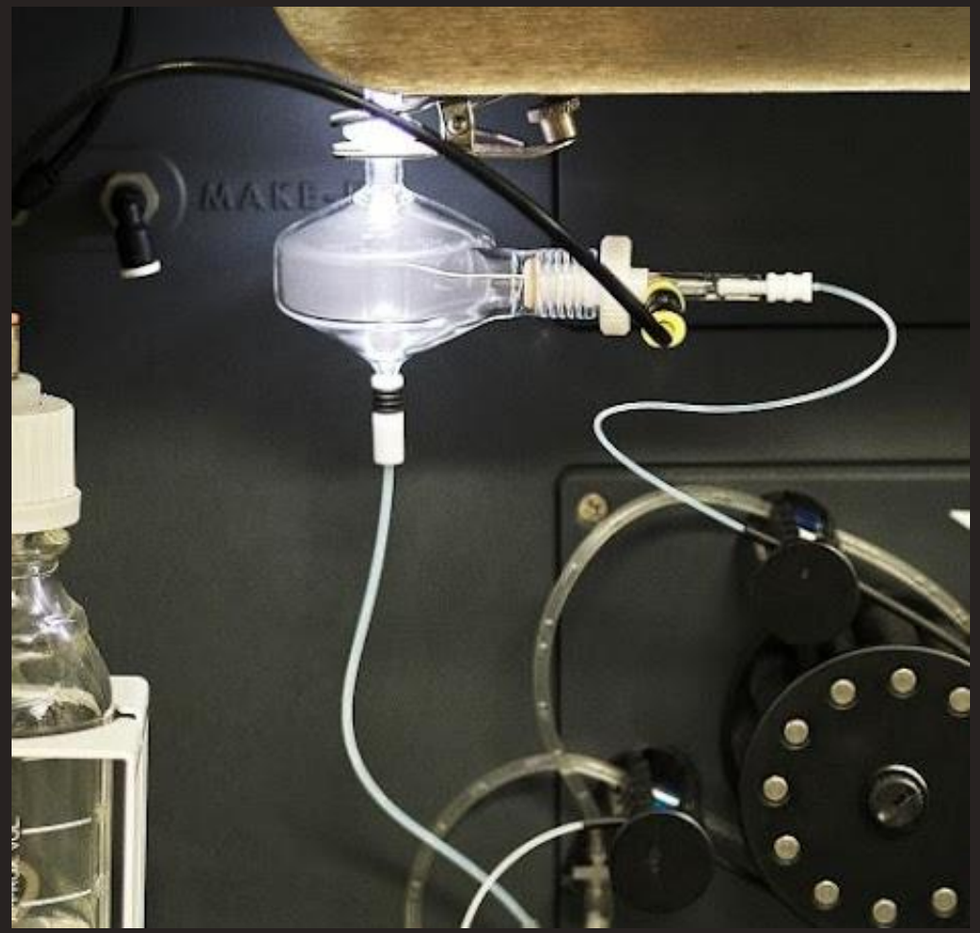
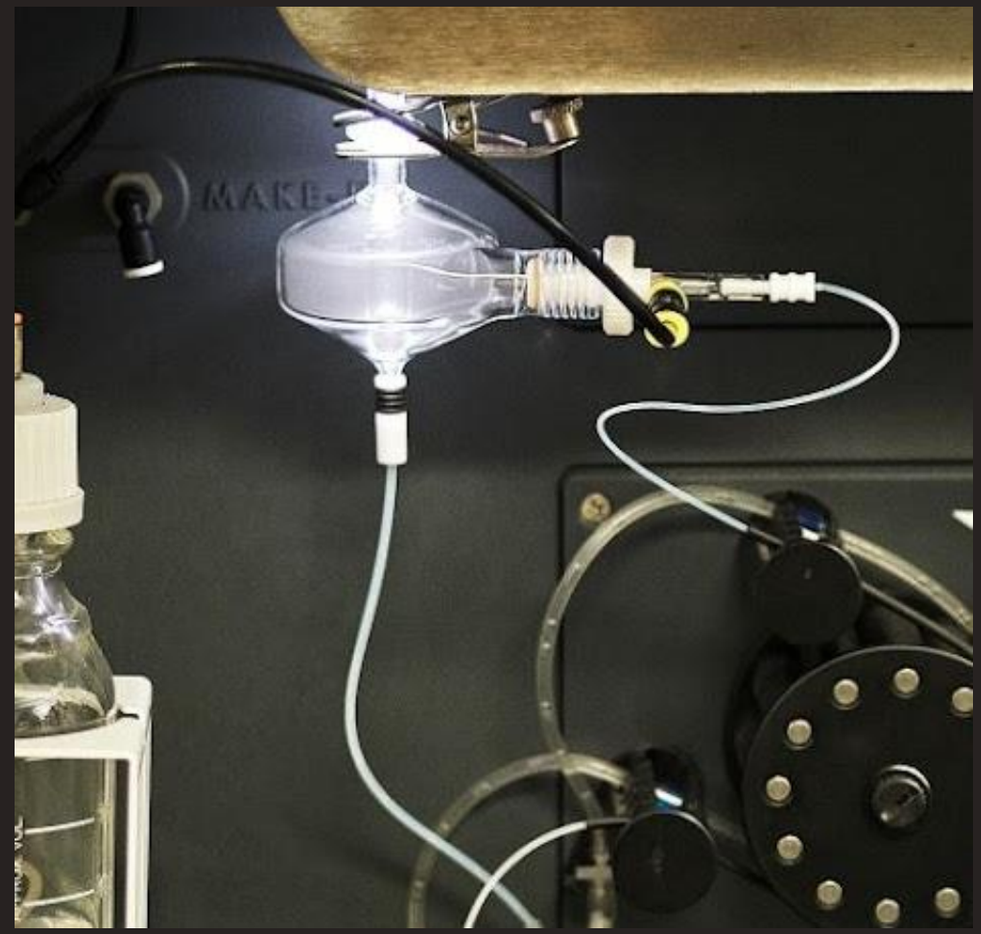


Nebulizer and Spray Chamber

- Affected by nebulizer geometry and gas flow rate
- High ionic content affects droplet size distribution and solvent evaporation
- Changes amount of sample being measured



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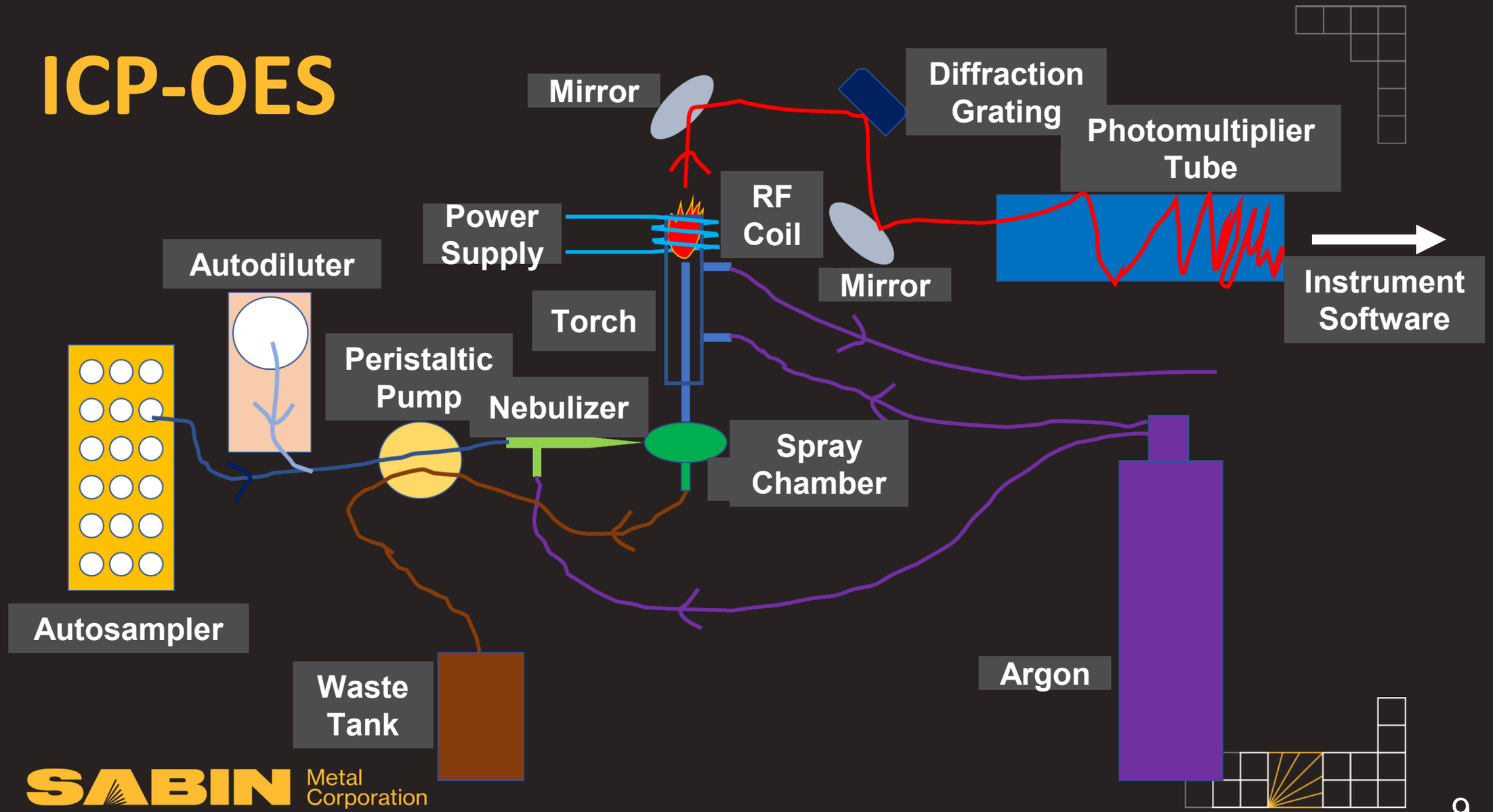

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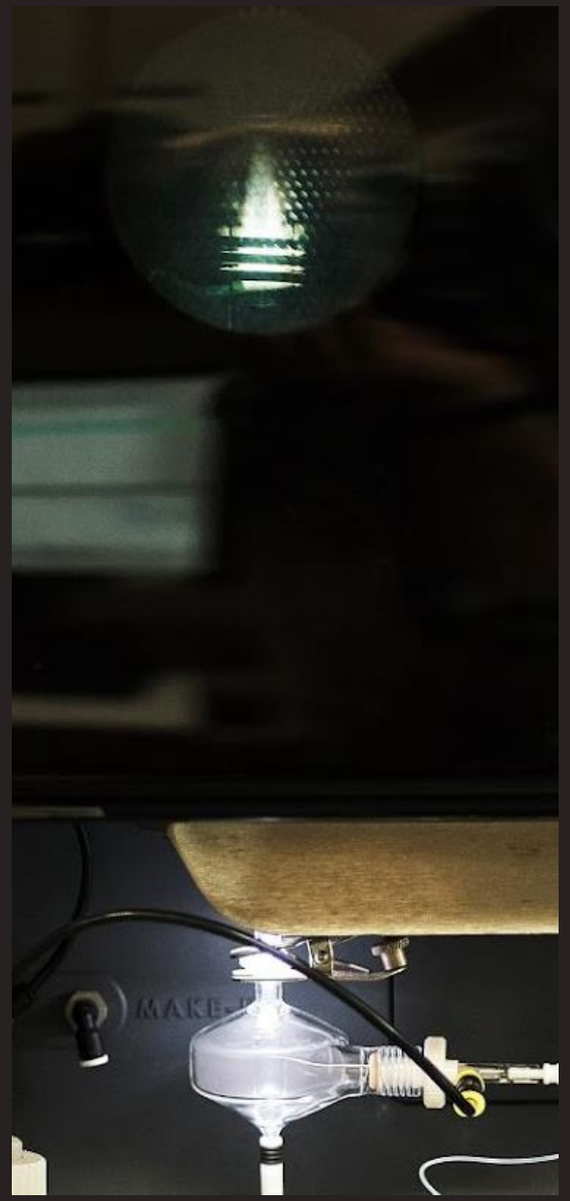
Plasma and Ionization

Plasma is generated by radio frequency power source and coil (~10,000K)

Superheating of sample ionizes elements

Ionized elements emit light at characteristic wavelengths



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Plasma and Ionization

Temperature gradient in plasma

└> Produces ionization gradient

Different elements have different ionization energies

Elements ionize at different plasma heights

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Plasma and Ionization

Matrix differences affect the ionization of the sample

Easily-Ionizable Elements (EIEs) shift the ionic gradient in the plasma

Can mitigate with ionization buffers or internal standards

Element	Ionization Energy (kJ/mol)
Cs	376
K	419
Na	496
Al	578
Pd	804
Pt	870
Au	890

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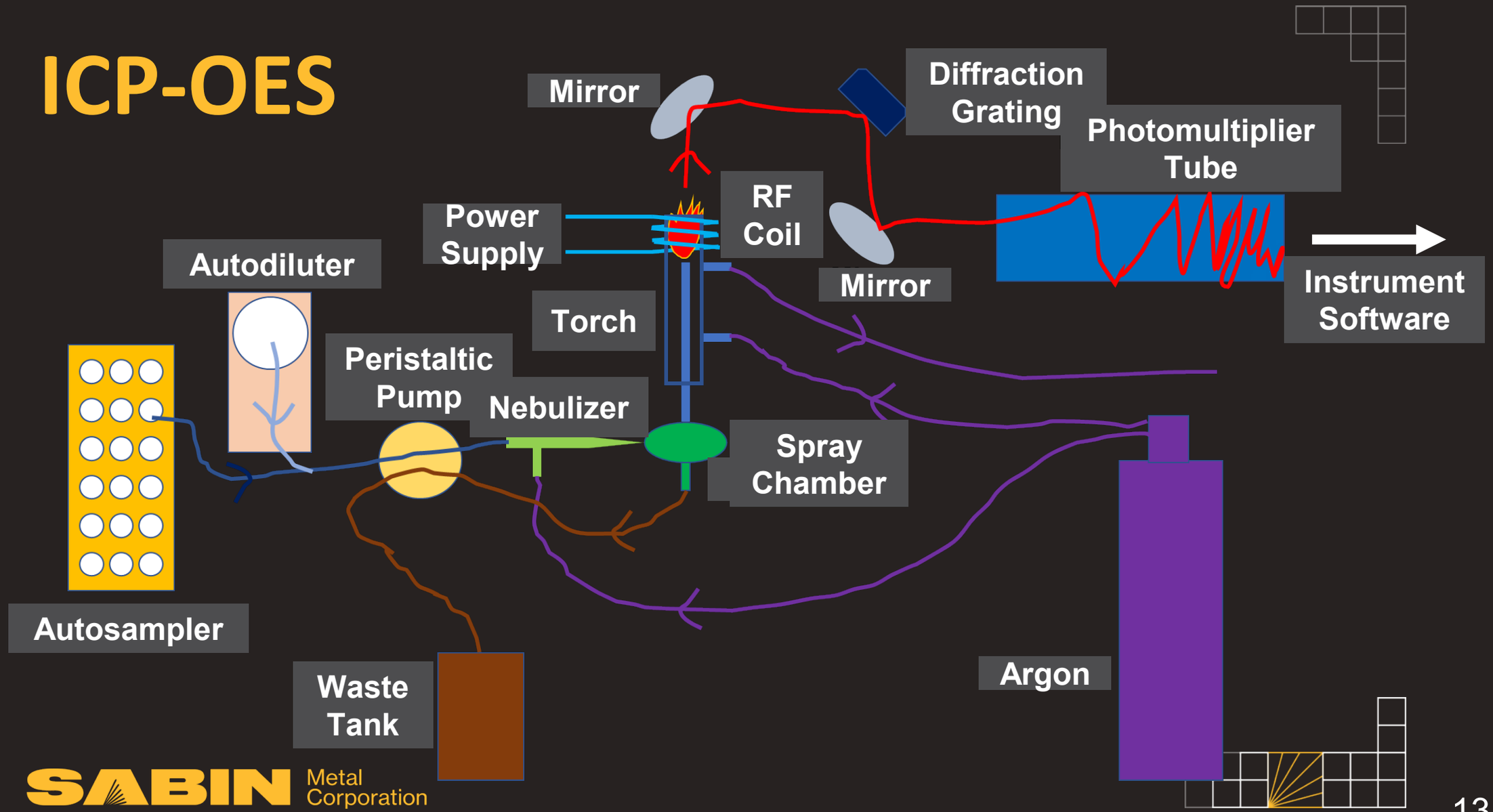

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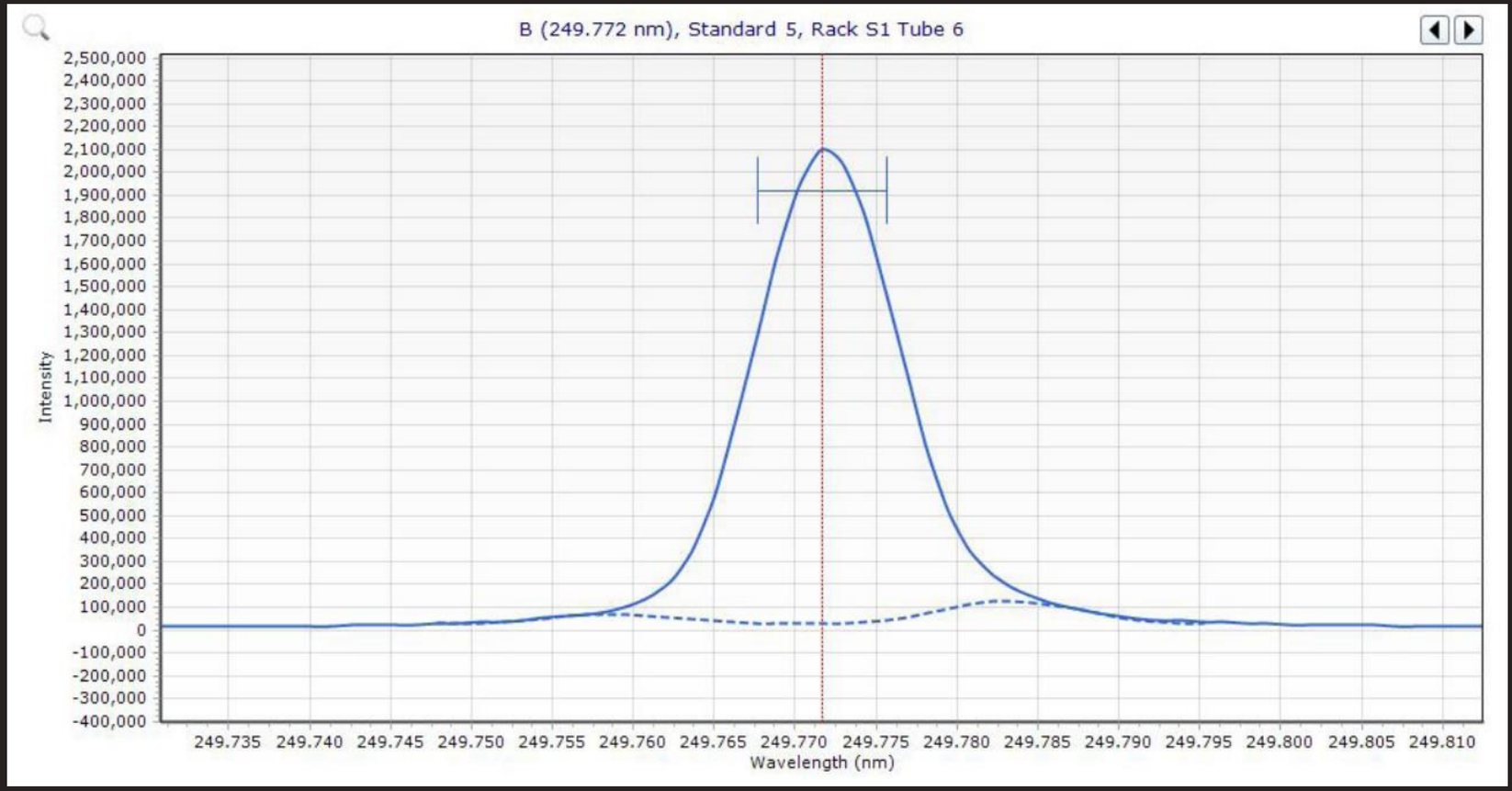
Measurement and Analysis



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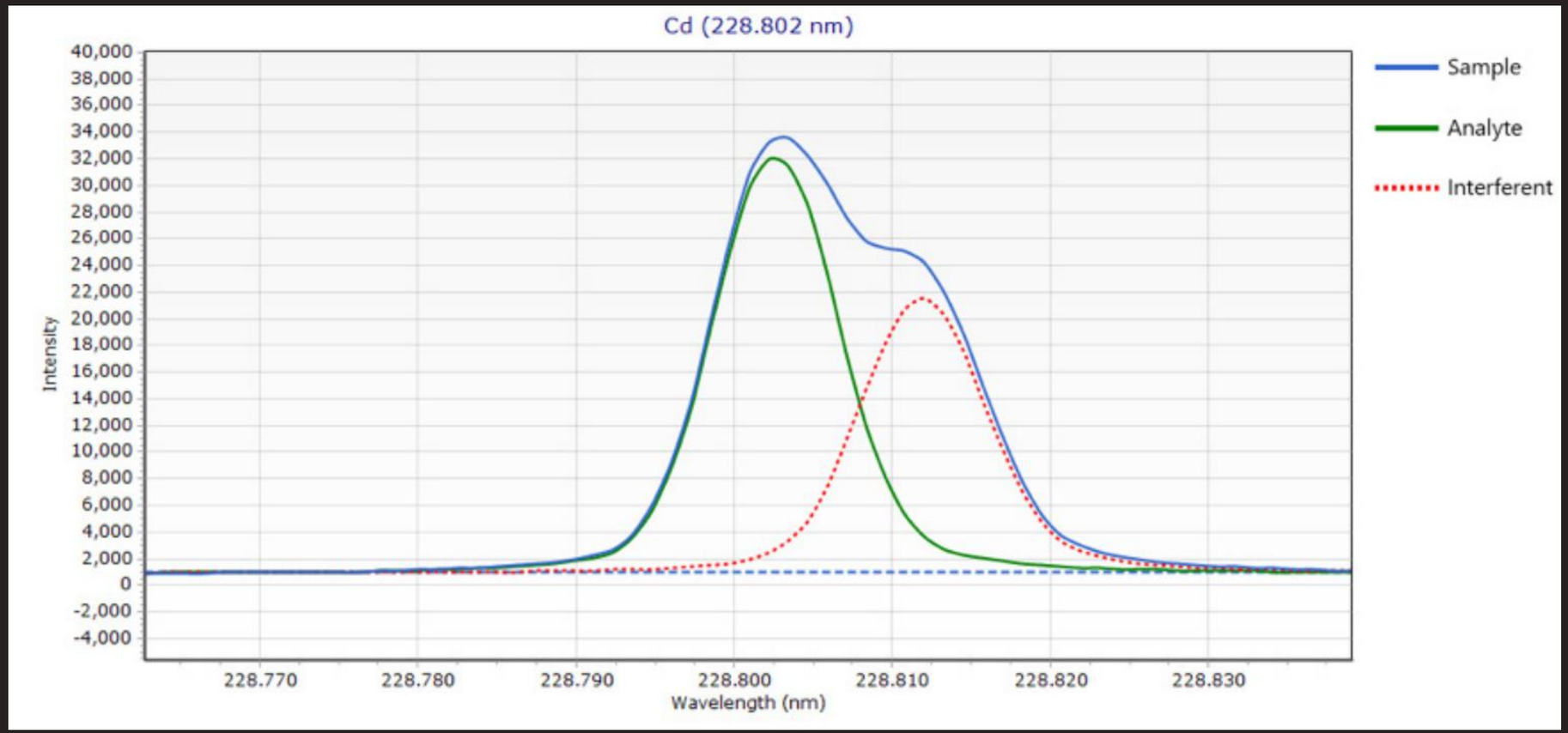
Measurement and Analysis



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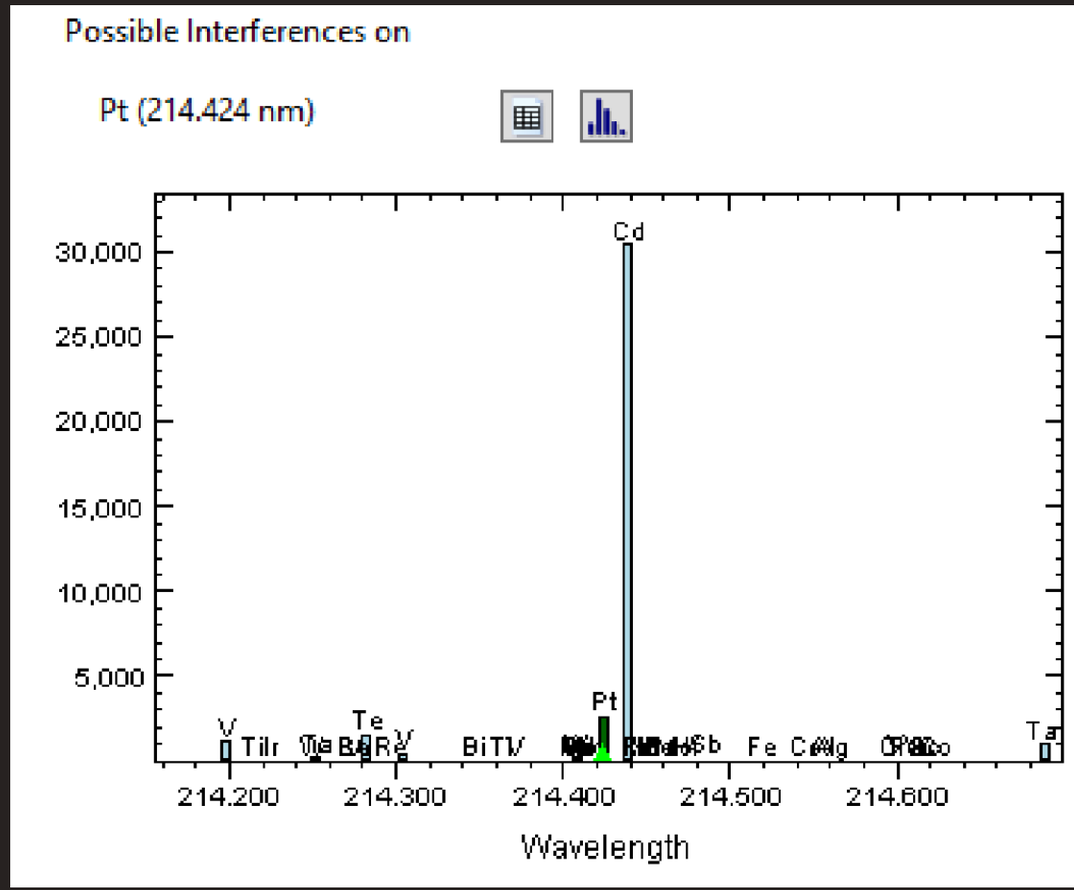
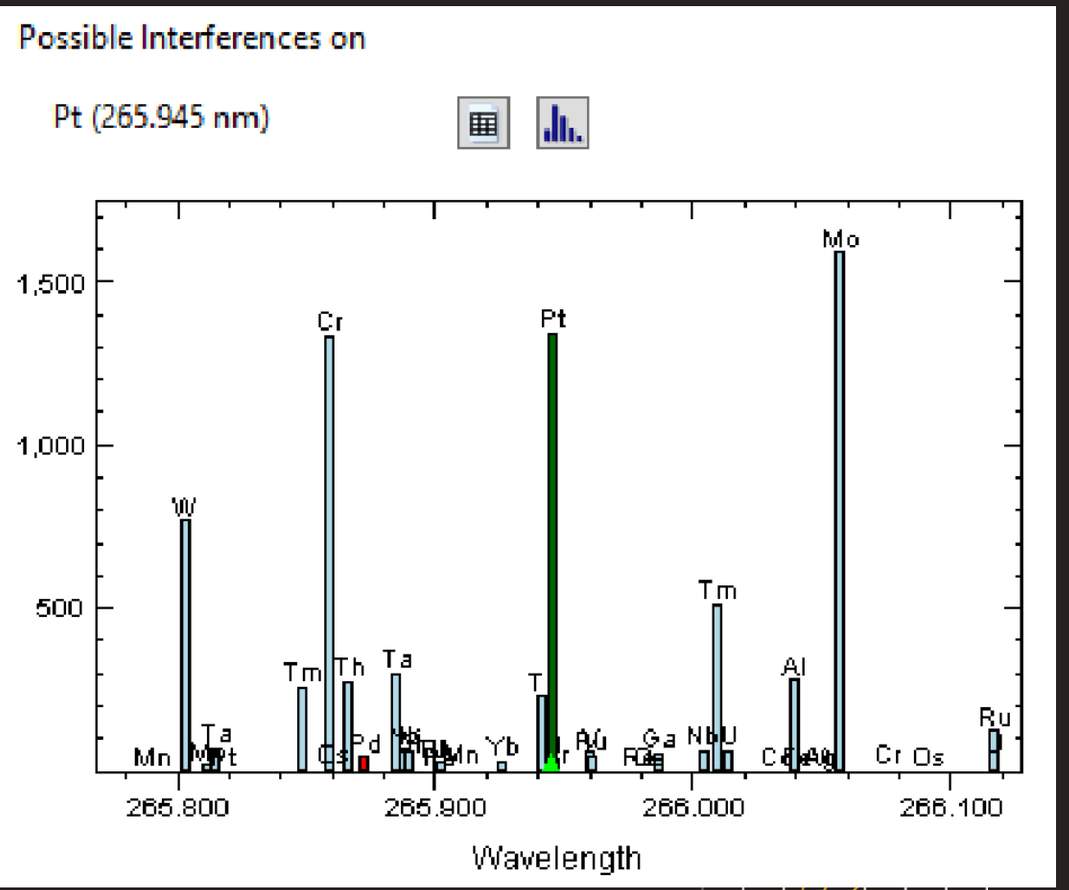
Measurement and Analysis





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Measurement and Analysis

For a solution containing 20 ppm Platinum:

Fe (ppm)	193.9nm	214.4nm	217.4nm	265.9nm	299.7nm
0	20.11	20.00	19.99	20.01	19.90
1000	19.58	18.48	19.96	22.79	20.77

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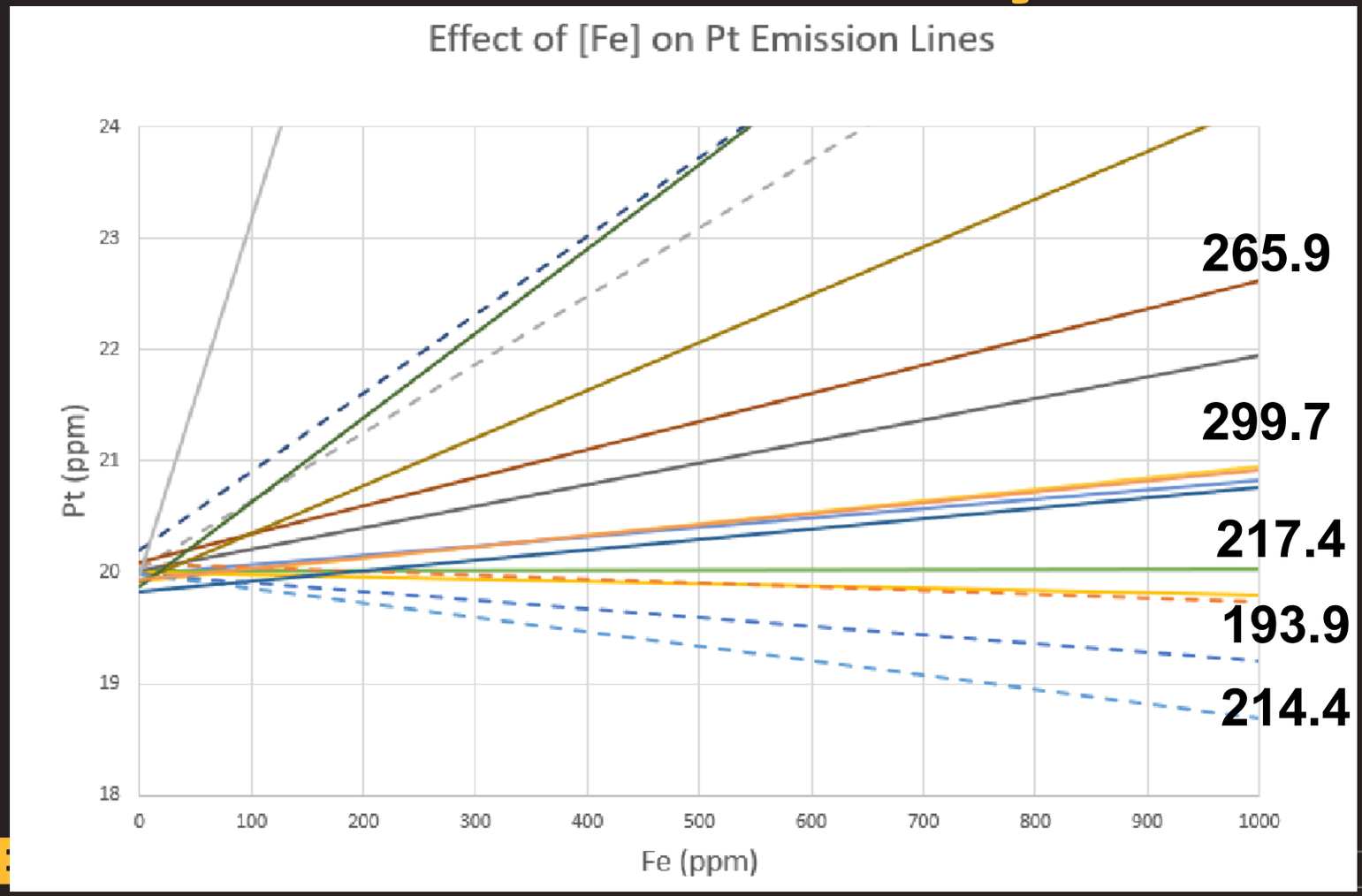
Measurement and Analysis



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0	20.11	20.00	19.99	20.01	19.90
1000	19.58	18.48	19.96	22.79	20.77

How can we account for this?

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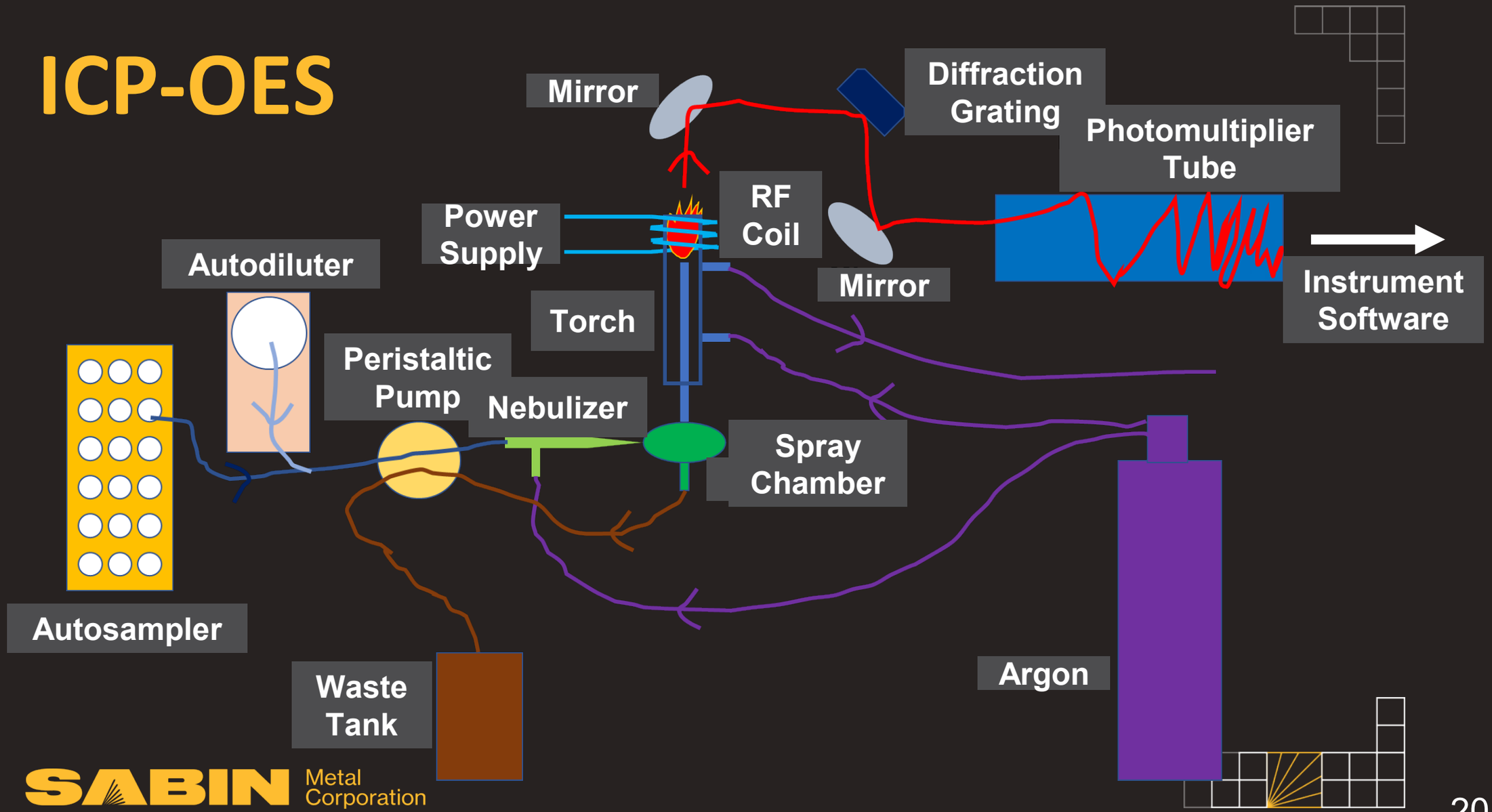

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Statistical Modeling

Observe and quantify effects under controlled conditions

Create model that describes effect

Validate the model with test solutions

Treat matrix effects symptomatically

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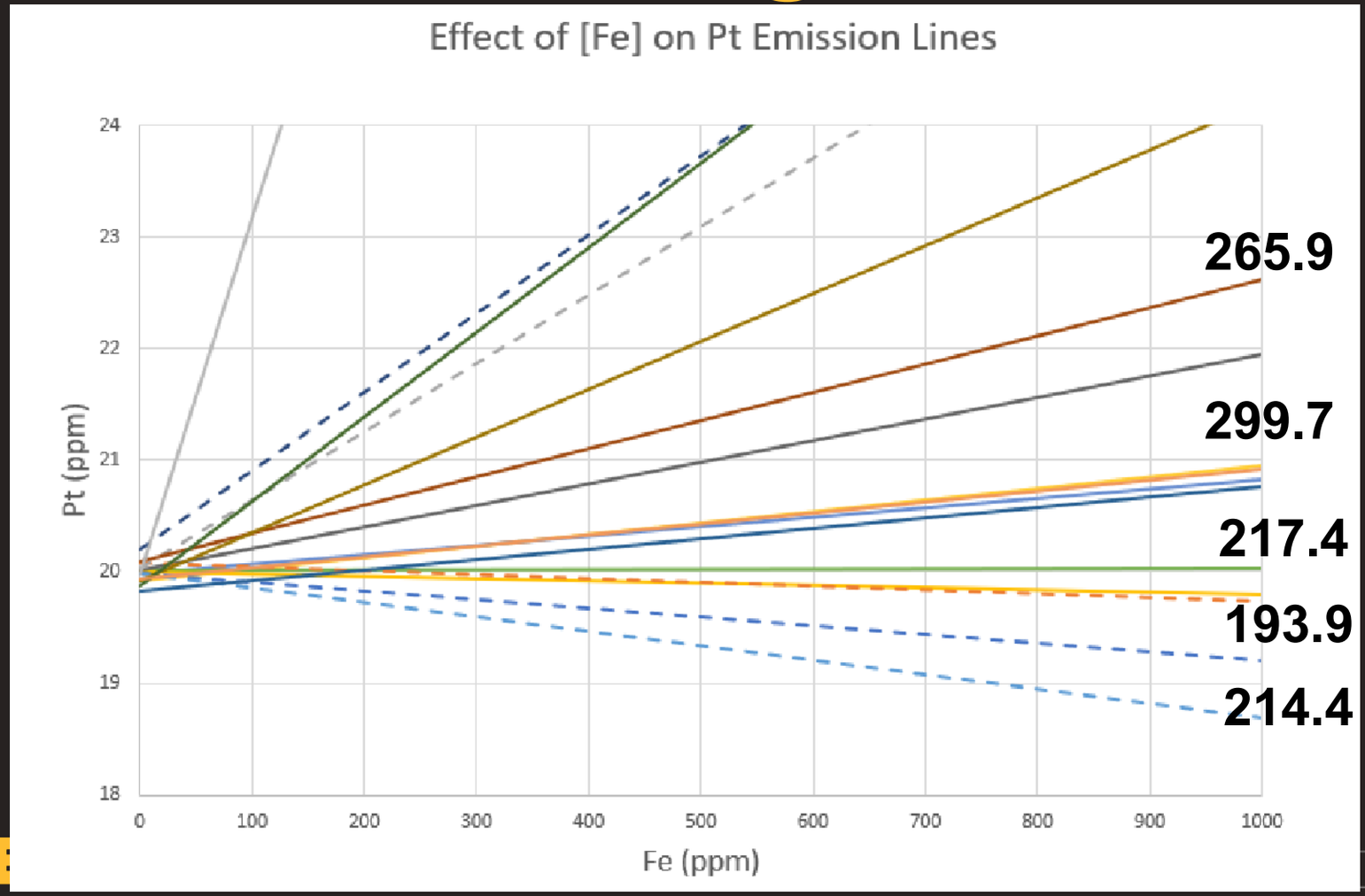
Statistical Modeling



Statistical Modeling

	203.6nm	214.4nm	217.4nm	265.9nm	299.7nm
slope (ppb)	-0.340	-1.294	0.019	2.520	0.981

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Statistical Modeling

Solution containing 20ppm Pt and 3000ppm Fe?

	203.6nm	214.4nm	217.4nm	265.9nm	299.7nm
slope (ppb)	-0.340	-1.294	0.019	2.520	0.981
Measured	19.11	16.18	20.10	27.60	22.92

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Statistical Modeling

Solution containing 20ppm Pt and 3000ppm Fe?

	203.6nm	214.4nm	217.4nm	265.9nm	299.7nm
slope (ppb)	-0.340	-1.294	0.019	2.520	0.981
Measured	19.11	16.18	20.10	27.60	22.92
Corrected	20.12	20.06	20.05	20.03	19.98

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Design of Statistical Model

Analysis of petrocatalyst, Pt and Re on Al_2O_3

Powder is dissolved, PMs precipitated and redissolved

Solution samples contain varying amounts of Al and Fe

Al and Fe can affect Pt and Re measurement

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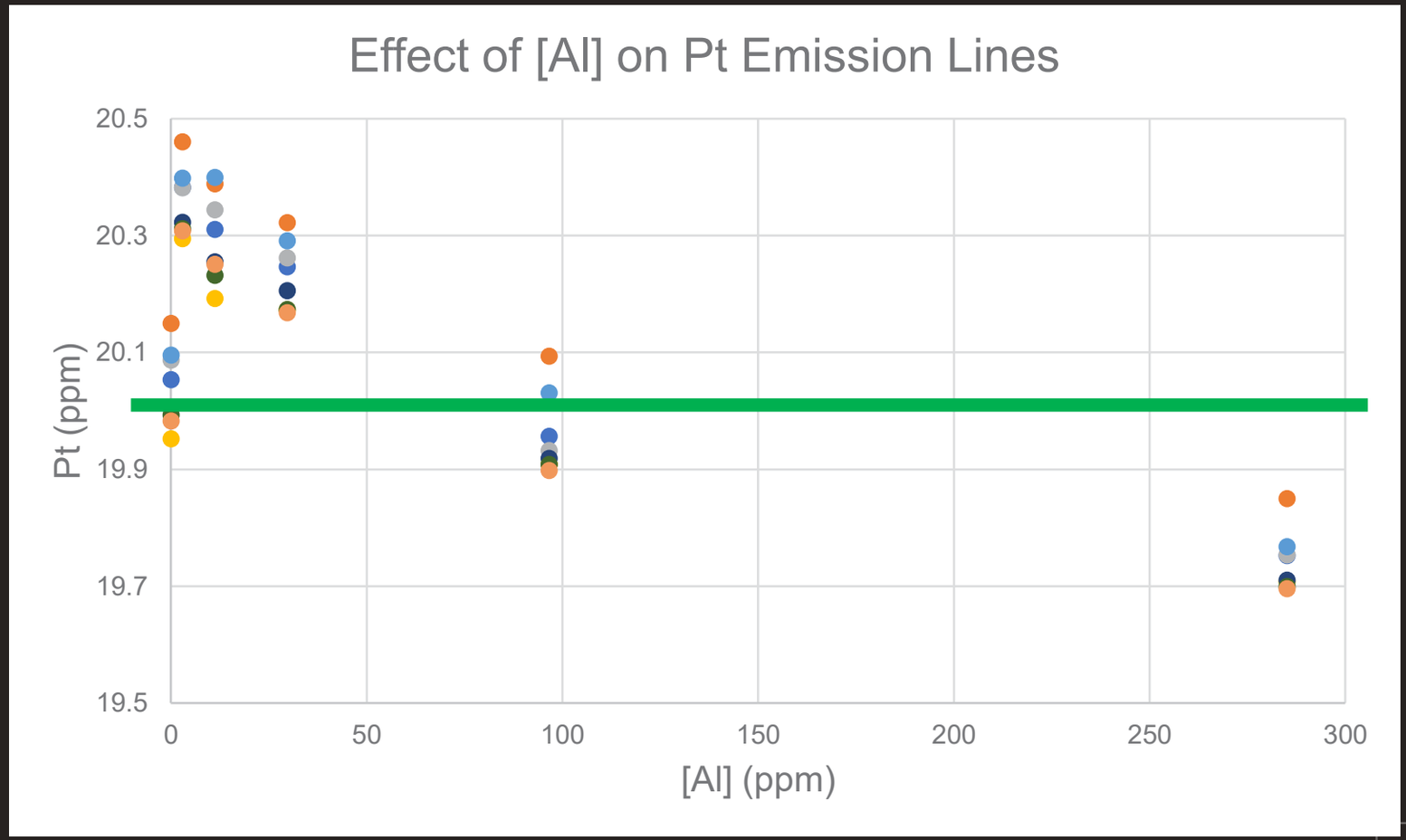
Design of Statistical Model



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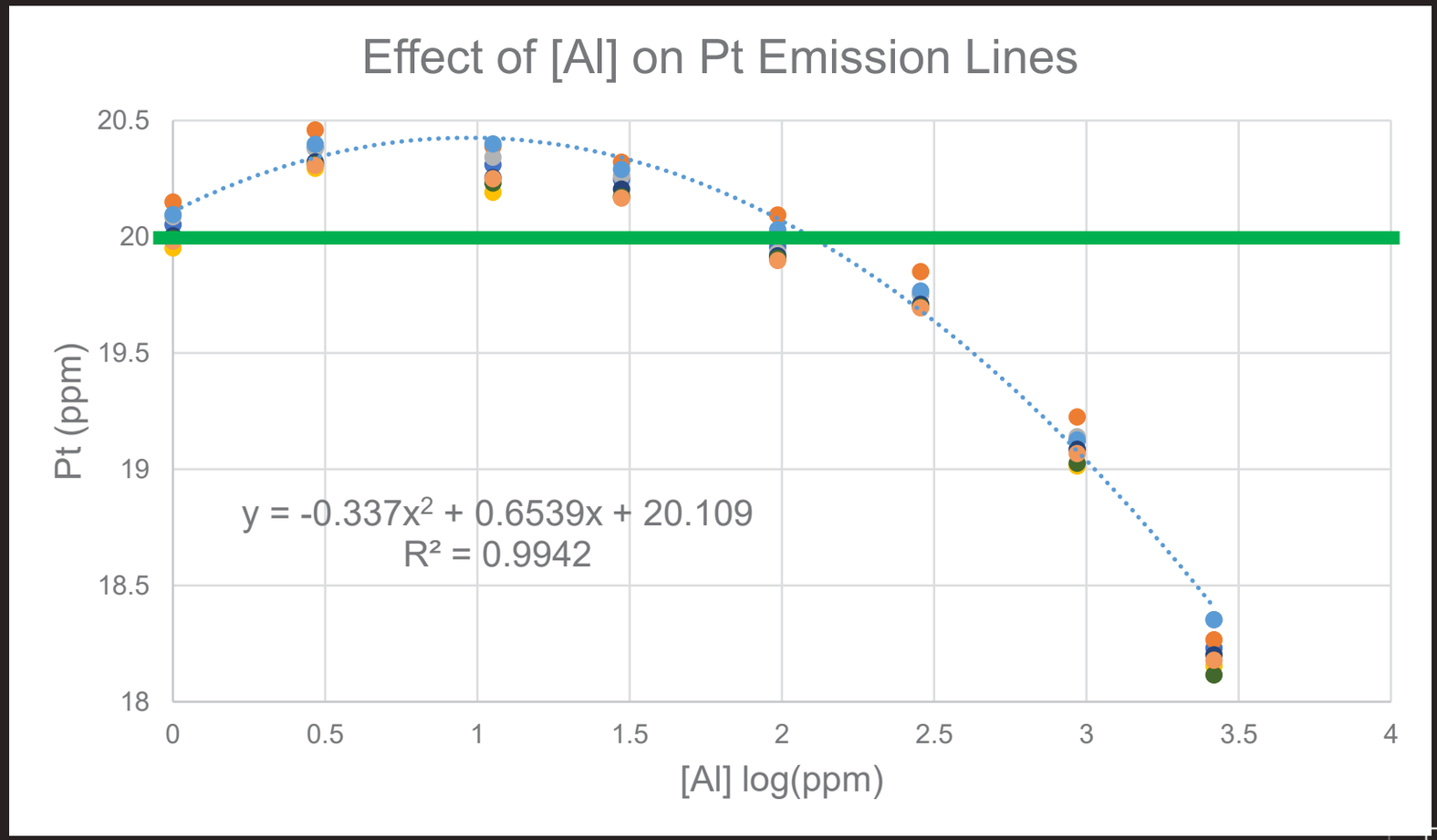
Design of Statistical Model



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Design of Statistical Model

Add both simple models together?

How do the Fe and Al interact as matrix effects?

Characterize and model the complex interaction

Create a response surface with statistical software

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Design of Statistical Model

Test solutions containing varied amounts of Al / Fe

0 / 0	0 / 25	0 / 50	0 / 75	0 / 100
3 / 0	3 / 25	3 / 50	3 / 75	3 / 100
10 / 0	10 / 25	10 / 50	10 / 75	10 / 100
30 / 0	30 / 25	30 / 50	30 / 75	30 / 100
100 / 0	100 / 25	100 / 50	100 / 75	100 / 100
300 / 0	300 / 25	300 / 50	300 / 75	300 / 100
1000 / 0	1000 / 25	1000 / 50	1000 / 75	1000 / 100

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Design of Statistical Model

Fit Summary

Response 17: Pt 265.9

	Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
	Linear	< 0.0001		0.5078	0.4251	
	2FI	0.8403		0.4926	0.3400	
	Quadratic	< 0.0001		0.7659	0.6710	
	Cubic	**0.0002**		**0.8832**	**0.8324**	**Suggested**
	Quartic	0.9574		0.8611	0.7010	
	Fifth	0.1328		0.8894	0.4662	**Aliased**

	Pt 265.9	=
	+0.038540	
	+0.584866	* Al
	+0.003271	* Fe
	-0.006136	* Al * Fe
	-0.573890	* Al^2
	+0.000088	* Fe^2
	+0.000459	* Al^2 * Fe
	+0.000045	* Al * Fe^2
	+0.172416	* Al^3
	-7.95995E-07	* Fe^3

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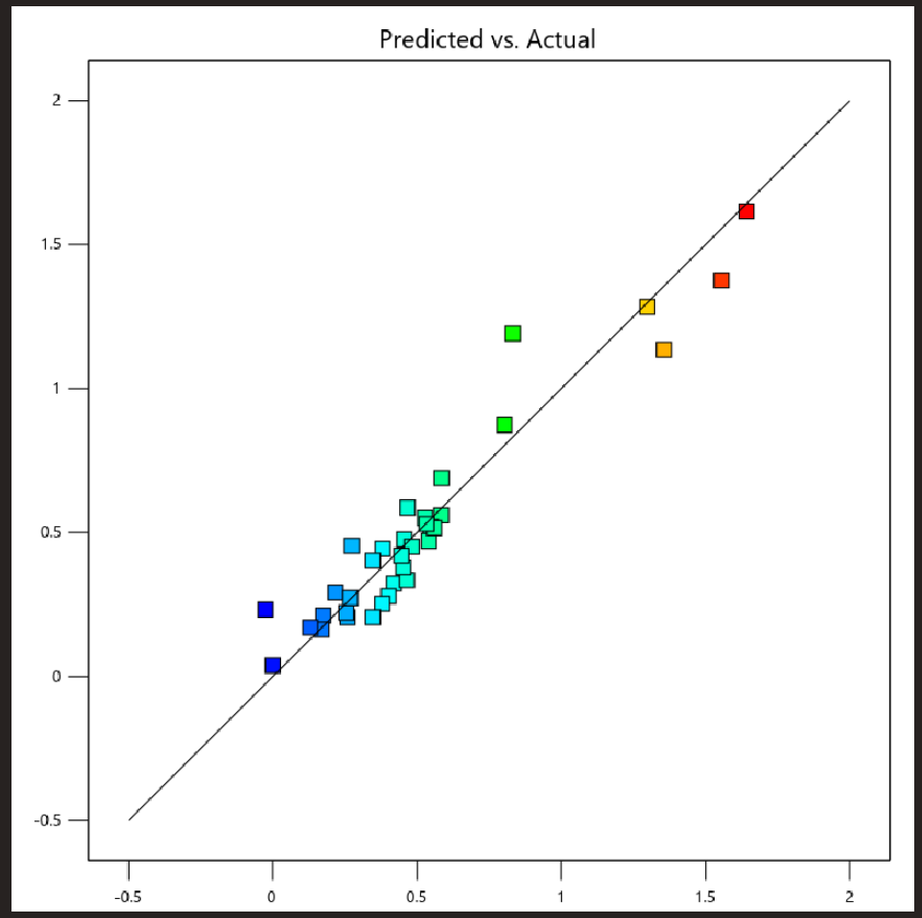
Design of Statistical Model



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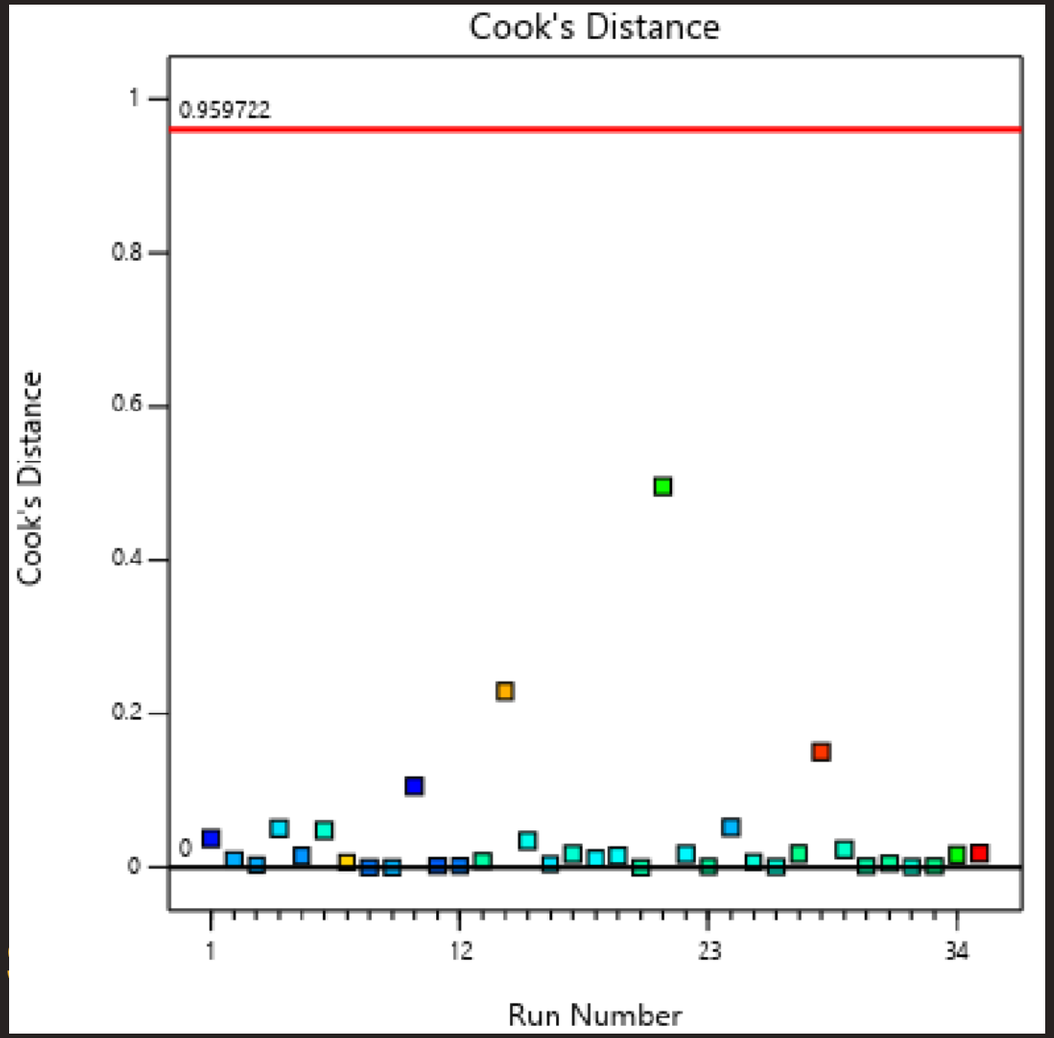
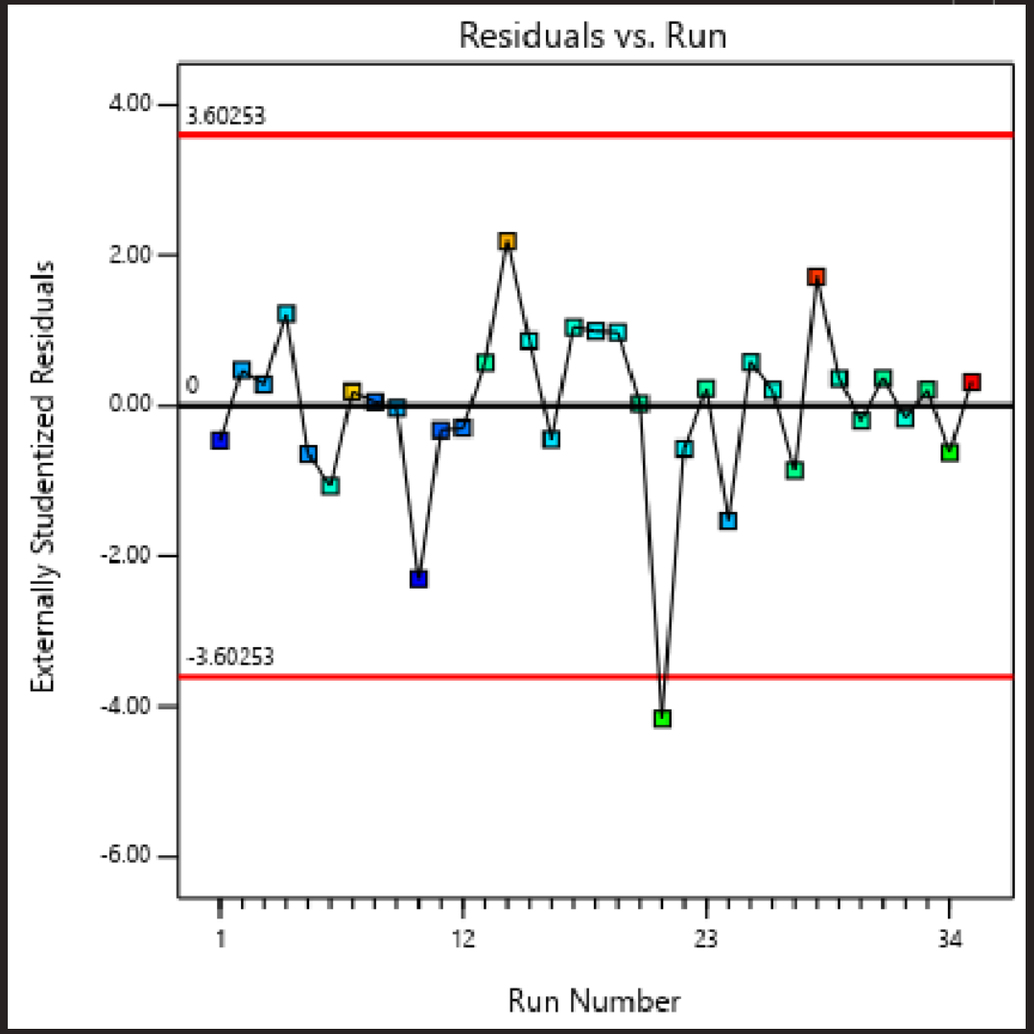
ANOVA for Cubic model

Response 17: Pt 265.9

	Source	Sum of Squares	df	Mean Square	F-value	p-value	
	Model	4.83	9	0.5364	29.57	< 0.0001	significant
	A-Al	0.0388	1	0.0388	2.14	0.1561	
	B-Fe	0.0926	1	0.0926	5.10	0.0328	
	AB	0.0031	1	0.0031	0.1735	0.6805	
	A^2	1.33	1	1.33	73.23	< 0.0001	
	B^2	0.0500	1	0.0500	2.76	0.1094	
	A^2B	0.0069	1	0.0069	0.3807	0.5428	
	AB^2	0.0772	1	0.0772	4.26	0.0496	
	A^3	0.5014	1	0.5014	27.64	< 0.0001	
	B^3	0.0156	1	0.0156	0.8595	0.3628	
	Residual	0.4536	25	0.0181			
	Cor Total	5.28	34				

Design of Statistical Model

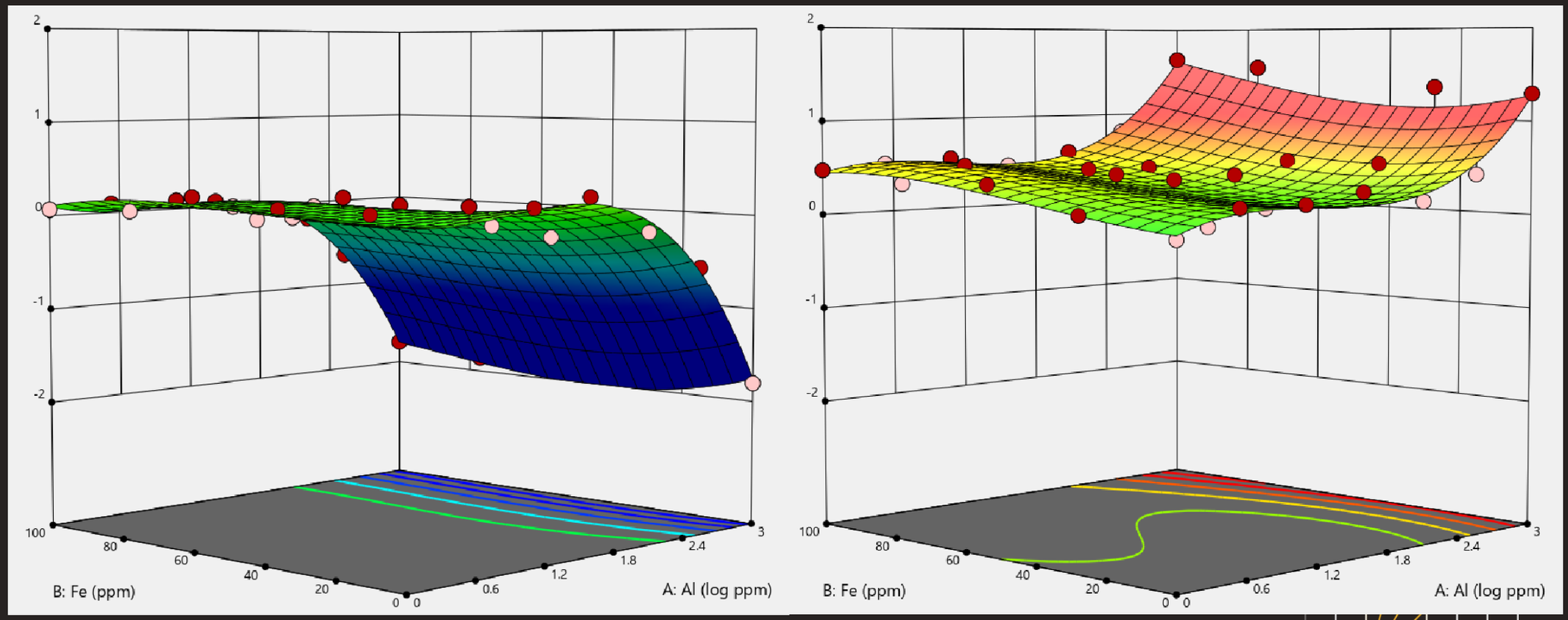




Design of Statistical Model

Pt 214.4nm

Pt 265.9nm



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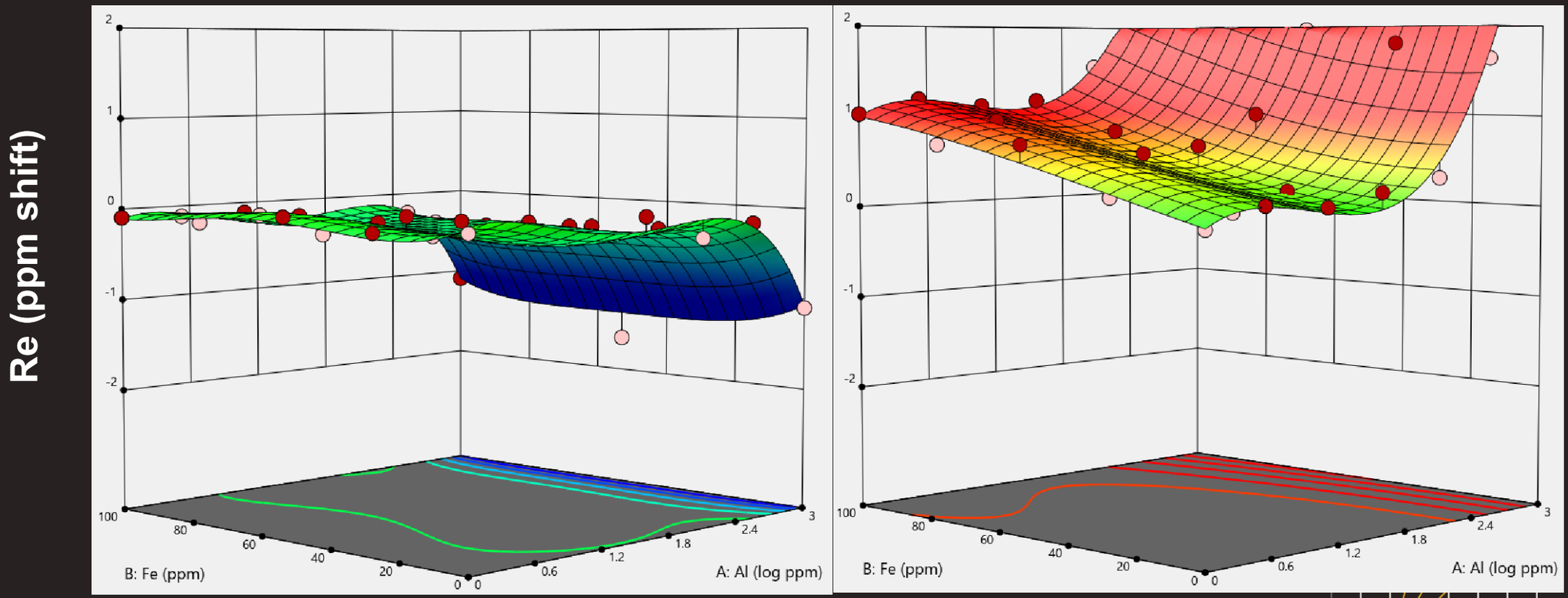
Design of Statistical Model

Re 221.4nm

Re 229.4nm



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Validating the Model

Composition		As Measured		With Correction		
Al	Fe	Pt Median	% Error	Pt Median	% Error	Error Reduction
20	100	20.34	1.71	20.04	0.19	**88.6**
30	70	20.40	2.01	20.17	0.84	**58.3**
4	80	20.36	1.81	19.99	-0.04	**97.8**
4	30	20.38	1.88	20.09	0.44	**76.9**
600	10	20.49	2.47	20.03	0.16	**93.3**
800	80	21.08	5.40	20.35	1.77	**67.3**
8	50	20.48	2.39	20.18	0.90	**62.3**
800	0	20.94	4.71	20.35	1.75	**62.9**
20	70	20.41	2.06	20.15	0.76	**62.9**
1	30	20.40	2.02	20.21	1.05	**48.3**

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Validating the Model

Composition		As Measured		With Correction		
Al	Fe	Re Median	% Error	Re Mean6	% Error	Error Reduction
20	100	20.13	0.64	19.91	-0.47	**26.0**
30	70	20.16	0.81	19.98	-0.09	**89.2**
4	80	20.07	0.34	19.80	-1.00	**Increased**
4	30	20.19	0.95	20.04	0.19	**80.4**
600	10	21.77	8.87	20.55	2.77	**68.8**
800	80	22.38	11.89	20.34	1.70	**85.7**
8	50	20.13	0.65	19.97	-0.15	**77.2**
800	0	22.33	11.64	20.37	1.85	**84.1**
20	70	20.12	0.60	20.01	0.07	**88.3**
1	30	20.08	0.40	20.01	0.06	**84.4**

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Validating the Model

Real test solutions?

Microwave-digested sample

- Entire powder dissolved

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Validating the Model

Real test solutions?

Microwave-digested sample

Entire powder dissolved

Known		Measured				Corrected		% Error
Sample	%Pt	Al (ppm)	Fe (ppm)	%Pt	% Error	% Pt	% Error	Reduction
17135 (Pt)	0.9110	305	5.1	0.8767	3.77	0.8932	1.95	**48.2**
17190 (Pt)	0.2249	2307	3.5	0.1844	18.00	0.2215	1.51	**91.6**
17190 (Re)	0.2185	2307	3.5	0.1679	23.18	0.2045	6.40	**72.4**

Conclusions

Matrix effects are complex and difficult to resolve

Dependent on sample and instrument parameters

Effects can be modeled under controlled conditions

Models can be used to correct for matrix effects in ICP-OES analyses

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