Analyzing Precious Metals in Slag by XRF

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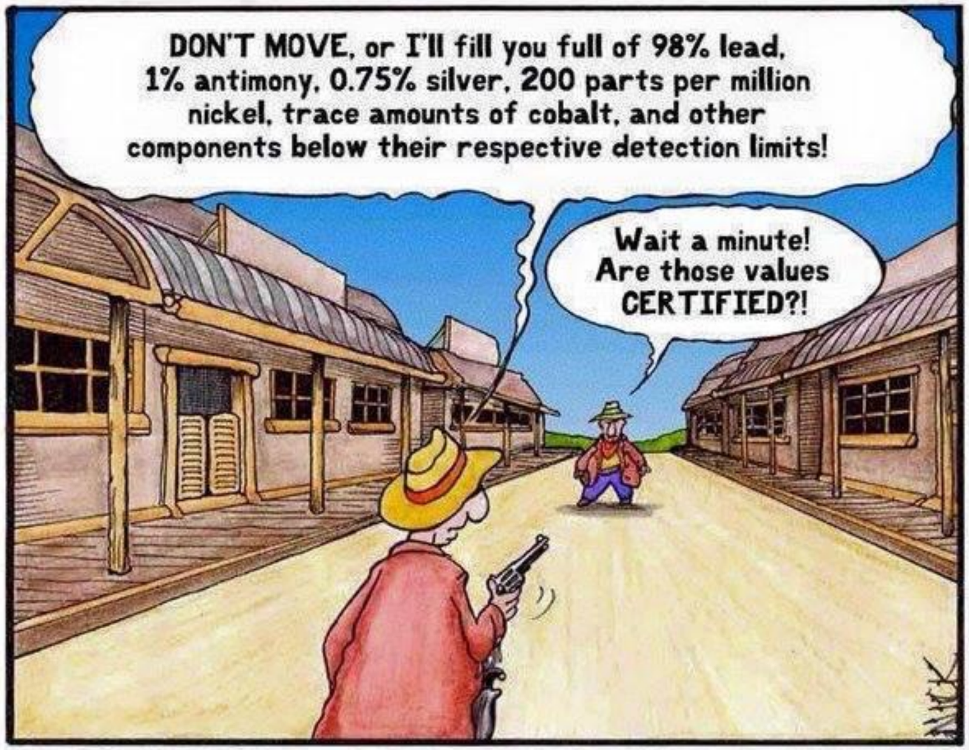
Introduction

- Run Slag containing precious metals (Pt and Pd)
- EDXRF vs WDXRF
- Sample Preparation
  - Loose Powder vs Pressed Pellet vs Fused Beads
- Qualitative, Quantitative & Analysis, Semi-Quantitative (Standardless)
- Conclusion



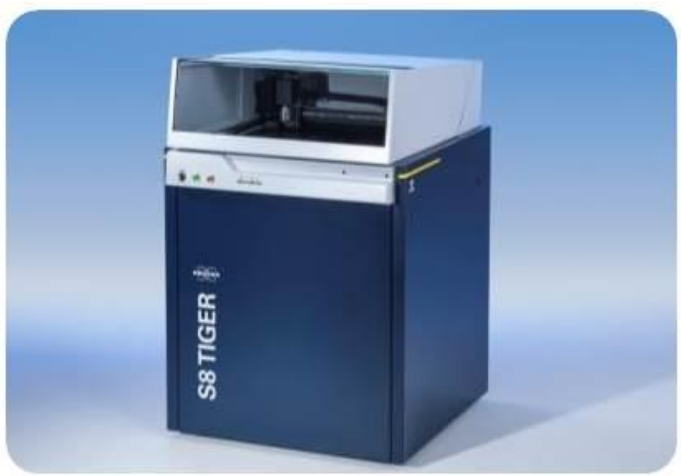
Analytical Chemists in the Wild West

EDXRF / WDXRF

X-Ray Fluorescence Instruments

EDXRF

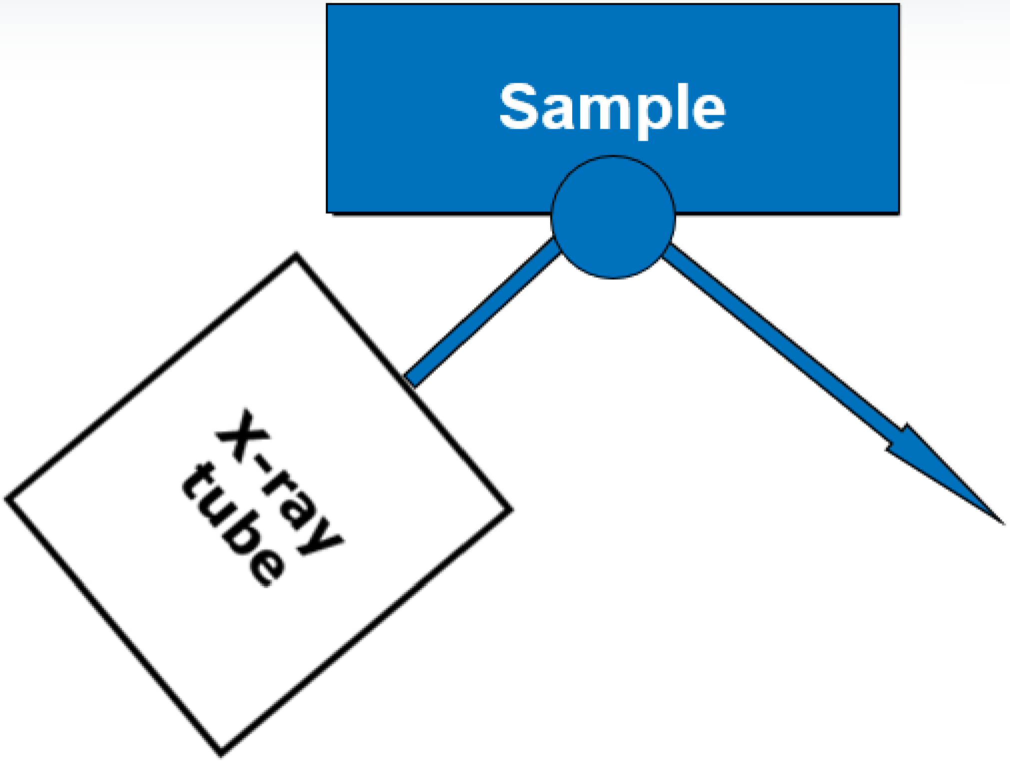
- Handheld
- ***Benchtop***
    - ***Direct Excitation***
    - Secondary Targets
    - Polarization
- Online



WDXRF

- Benchtop
- ***Floor Standing***
    - ***Sequential***
        - ***Mapping Option***
    - Simultaneous

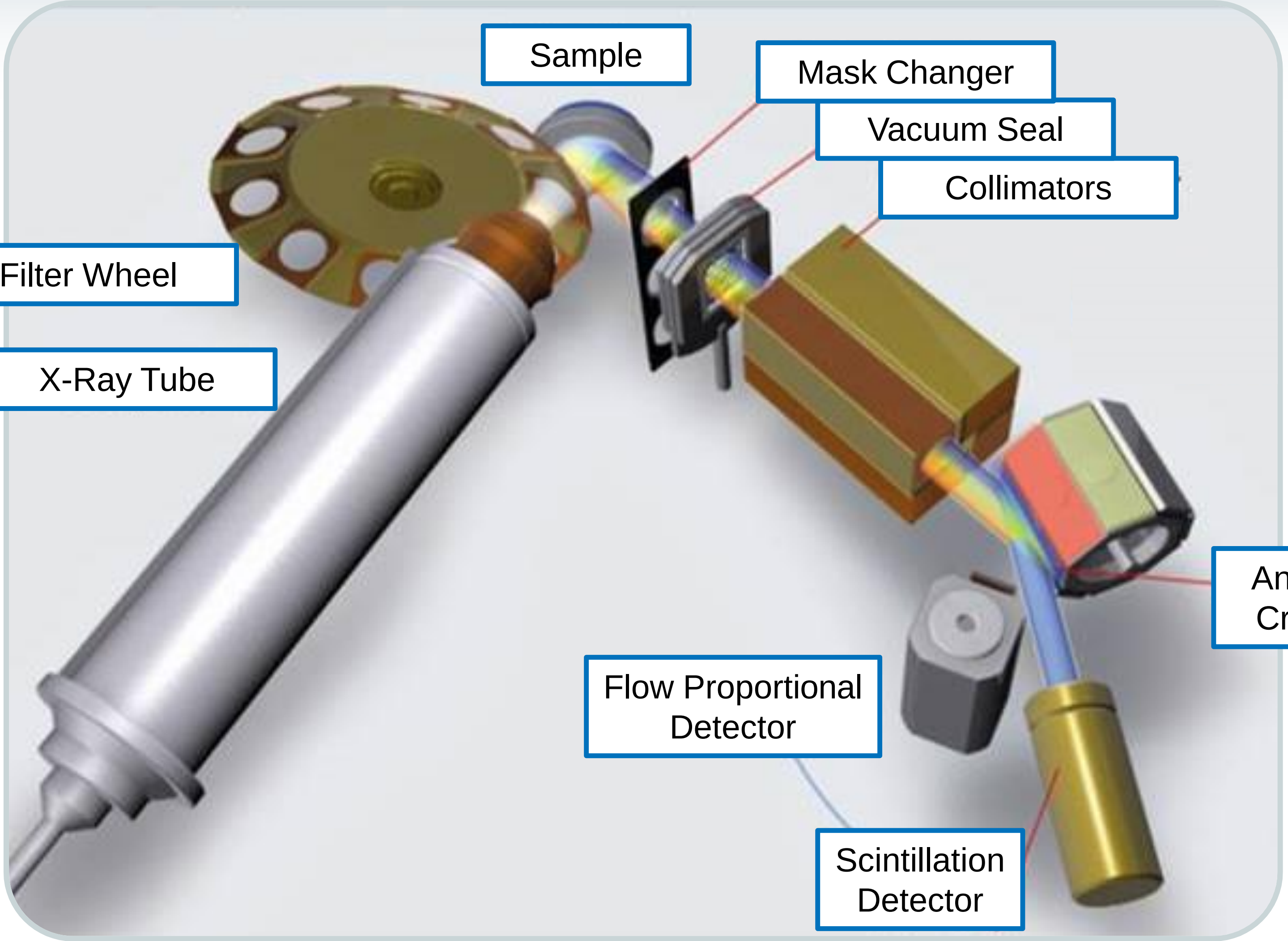
System Configuration
XRF



EDX
Detector only

WDX
Collimator
Analyzer Crystal
Detectors

System Configuration
WDXRF



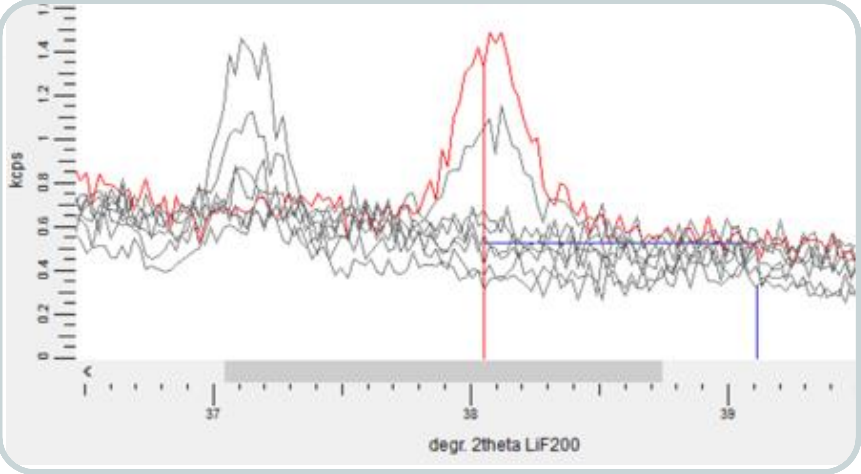
WDXRF Measurement Method
Slags

	Pd La	Re La	Pt La
Tube Voltage (kV)	50	50	50
Tube Current (mA)	20	20	20
Analyzer Filter	Cu 200µm	Al 100µm	Al 100µm
Collimator	0.23^{O}	0.46^{O}	0.23^{O}
Analyzer Crystal	LiF 200	LiF 200	LiF 200
Detector	Scint	Scint	Scint
Peak / Bkgd 2 Theta	16.680 15.059 15.824 18.971	38.052 39.113	41.742 43.885
Time (s) (Pk /Bkgd)	60/60	60/60	60/60

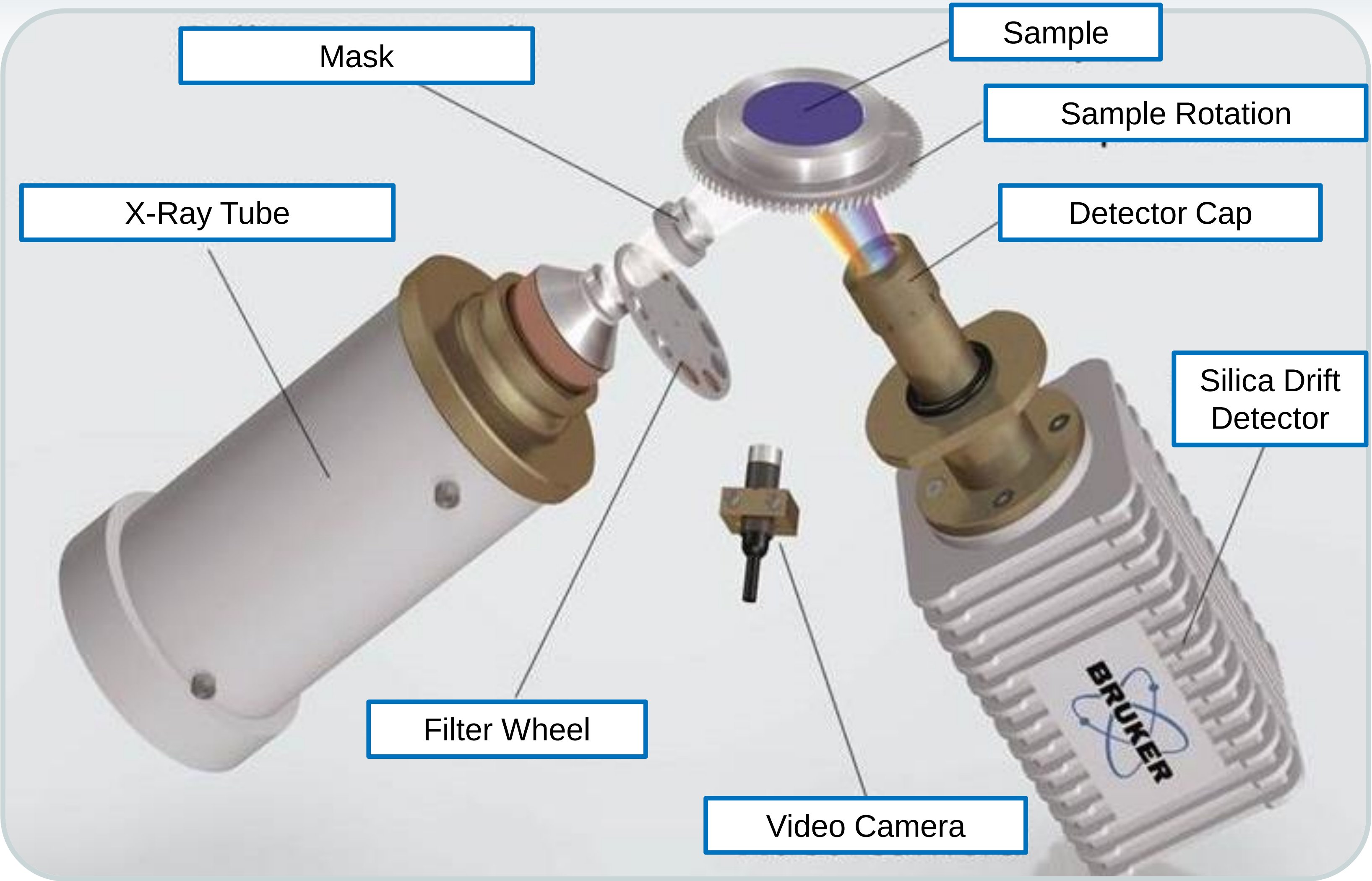
- Sample Rotation = On
  - (0.5 rev/sec)
- Mask Size = 34mm
- Measurement Mode:
  - Loose Powder
    - Helium
  - Pressed Pellet
    - Vacuum

WDXRF Measurement

Pt



System Configuration
EDXRF



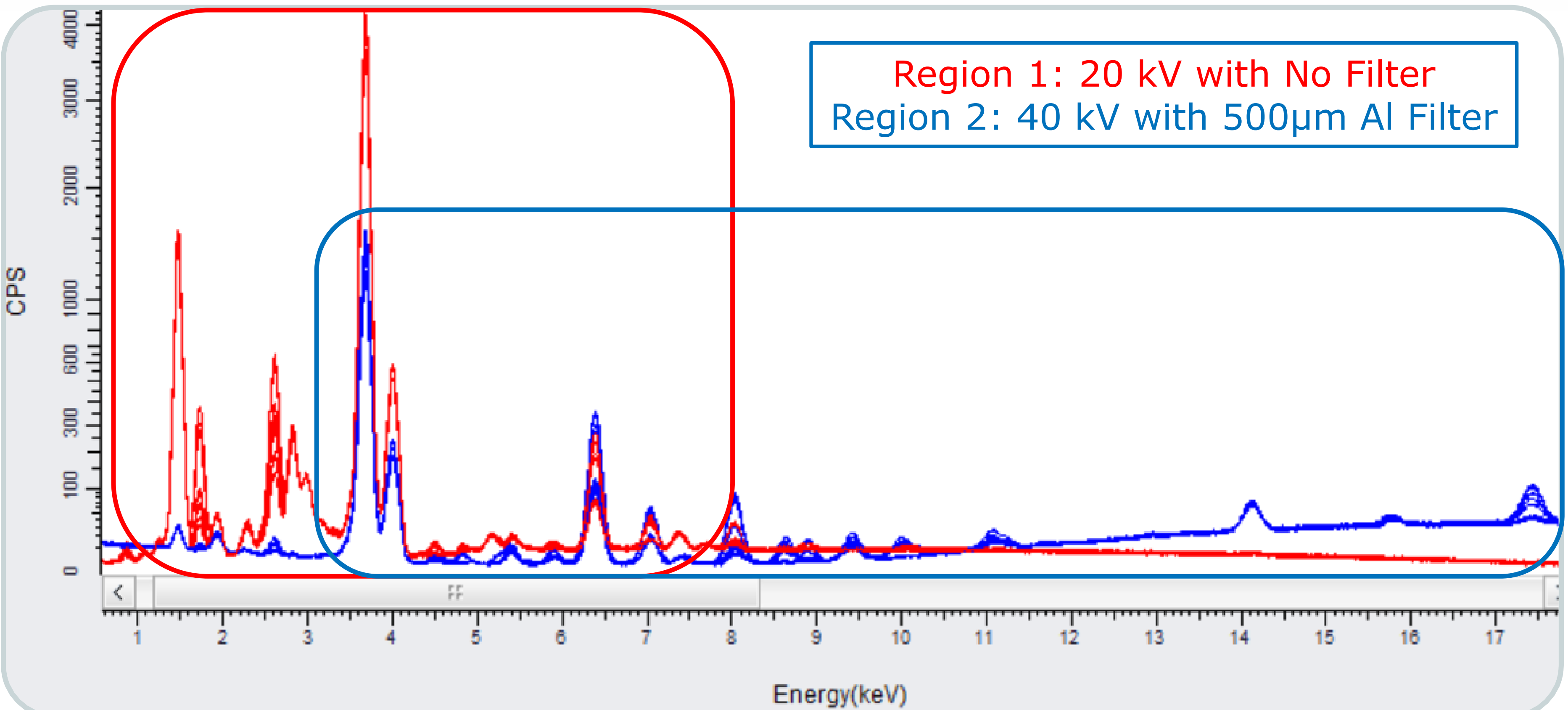
EDXRF Measurement Method
Slags

Range	Voltage (kV)	Current	Filter	Rate (cps)	Time (s)
Range 1	20 kV	Automatic	No Filter	100,000 cps	60 Seconds
Mg Kα, Al Kα, Si Kα, P Kα, S Kα, & Cl Kα					
Range 2	40 kV	Automatic	500 µm Al Filter	100,000 cps	120 Seconds
K Kα, Ca Kα, Ti Kα, Cr Kα, Mn Kα, Fe Kα, Sr Kα, Zr Kα, Cu Kα, Zn Kα, Pd Kα, Ce Lα, Re Lα & Lβ, & Pt Lα & Lβ					

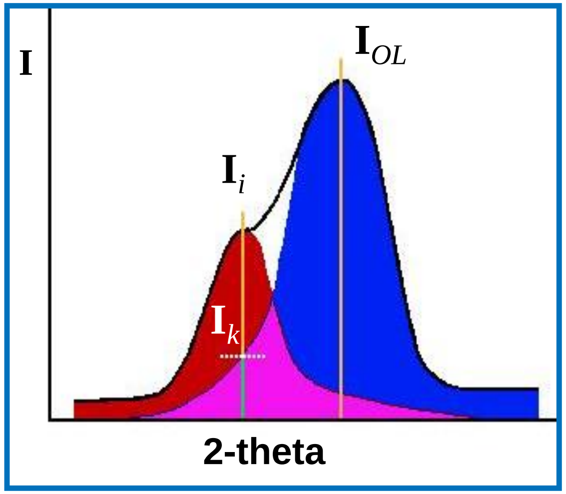
- Sample Rotation = On (0.5 rev/sec)
- Mask Size = 34mm

- Measurement Mode:
  - Loose Powder = Helium
  - Pressed Pellet = Vacuum

EDXRF
Measurement Regions

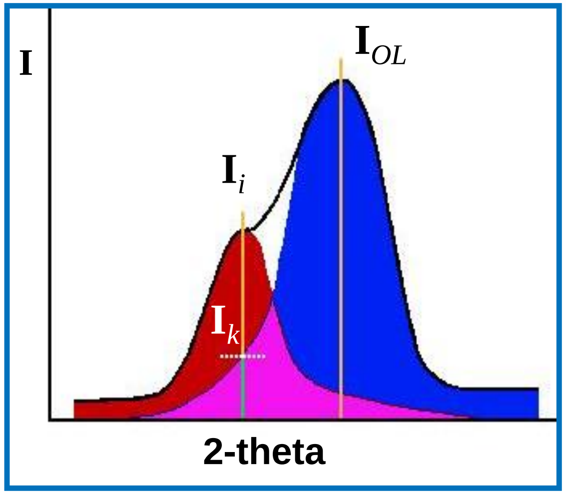


X-Ray Fluorescence Analysis Overlapping Elements



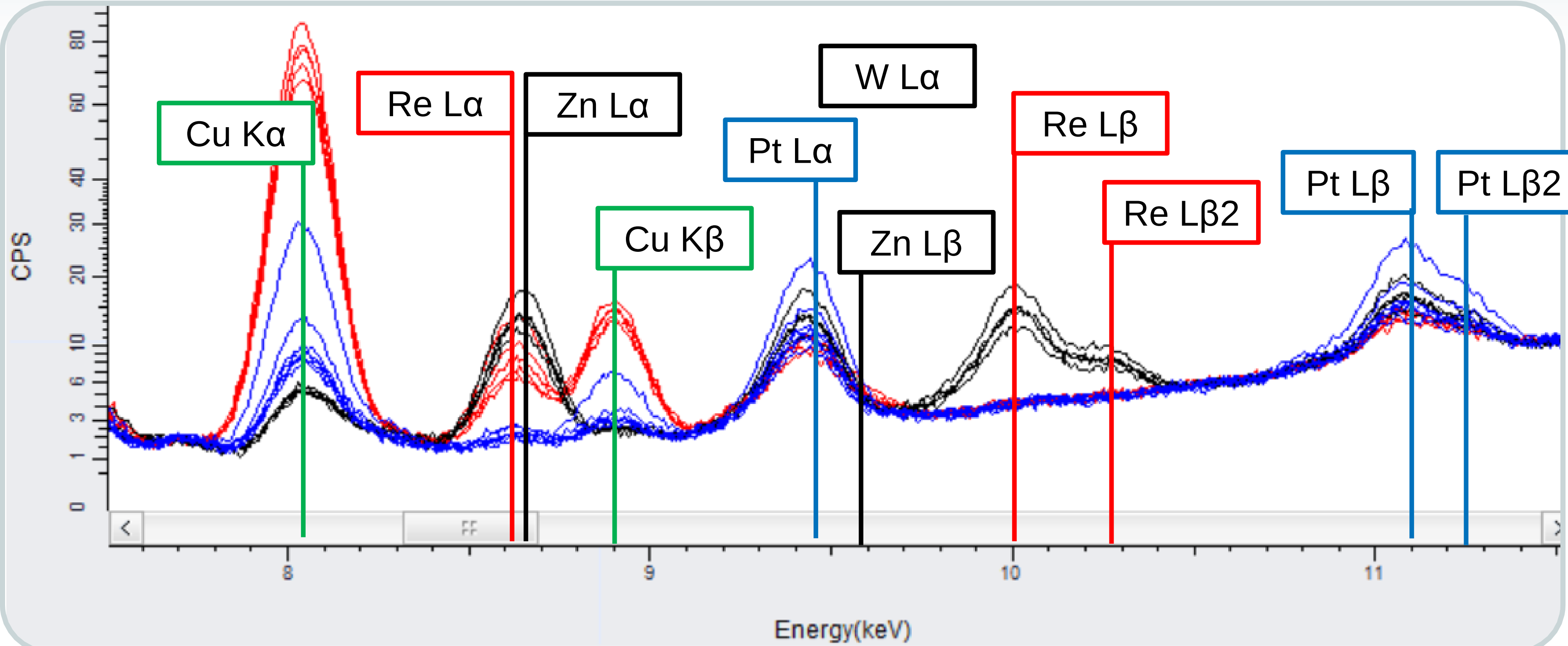
- The Element of Interest (I_i) has a contributing Intensity from another Element (I_{OL})
  - Another Element (Kα, Kβ, Lα, Lβ, etc..)
  - Sum Peaks
  - Escape Peaks
- The effect of this overlapping line (I_k) must be removed from the intensity of the element of interest (I_i) before concentrations are calculated.

X-Ray Fluorescence Analysis Overlapping Elements



- Before applying a line overlap correction we can also try one of the following:
    - Choose an Alternative Spectral Lines (i.e. Kβ, Lβ, etc...)
    - Choose another Analyzer Crystal or Finer Collimator (WDX)
    - Apply Mathematical Overlap Correction
        - Need Sufficient Number of Calibration Stds

EDXRF Spectra
40kV / 500µm Al Filter

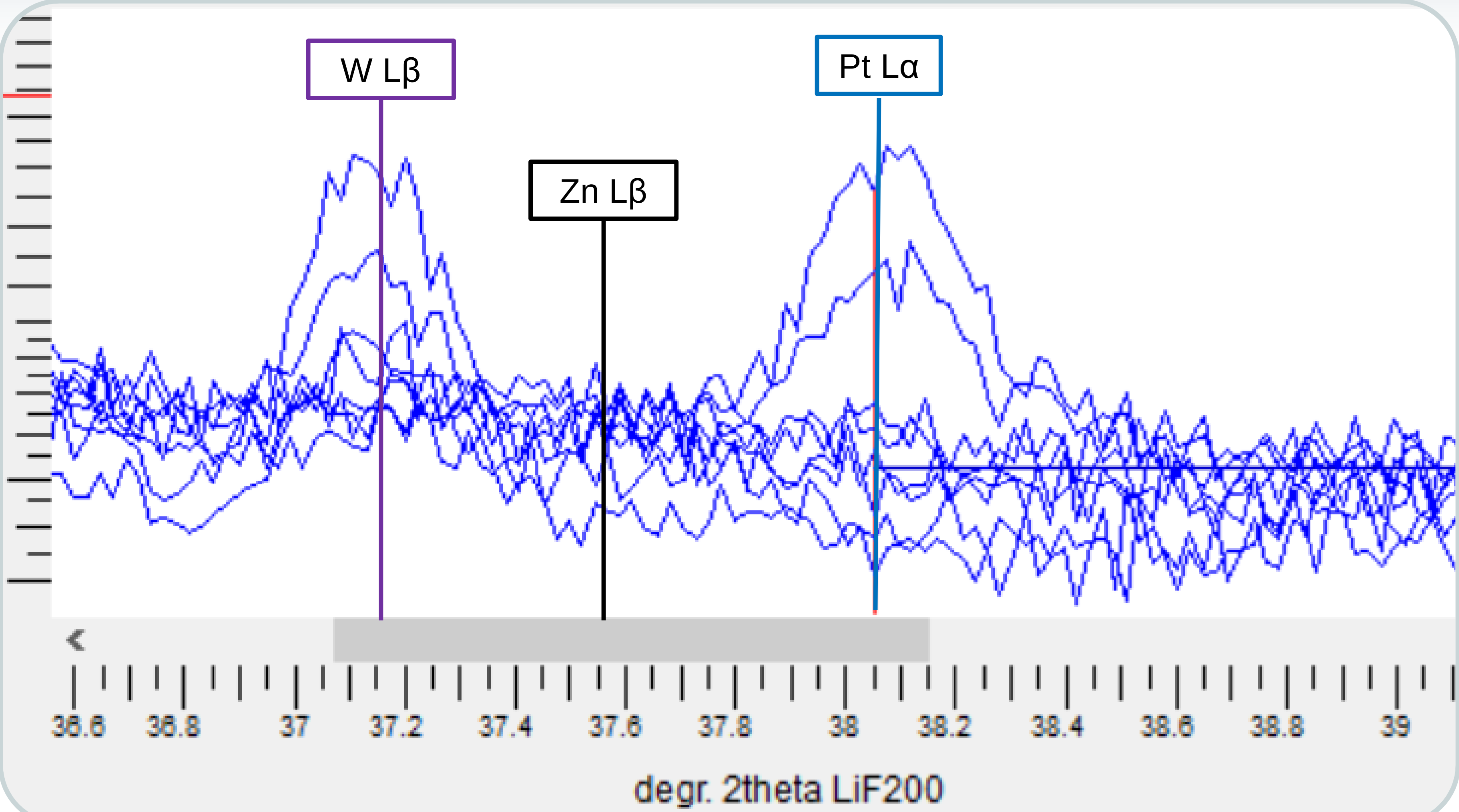


There are more spectral overlap with EDX vs WDX

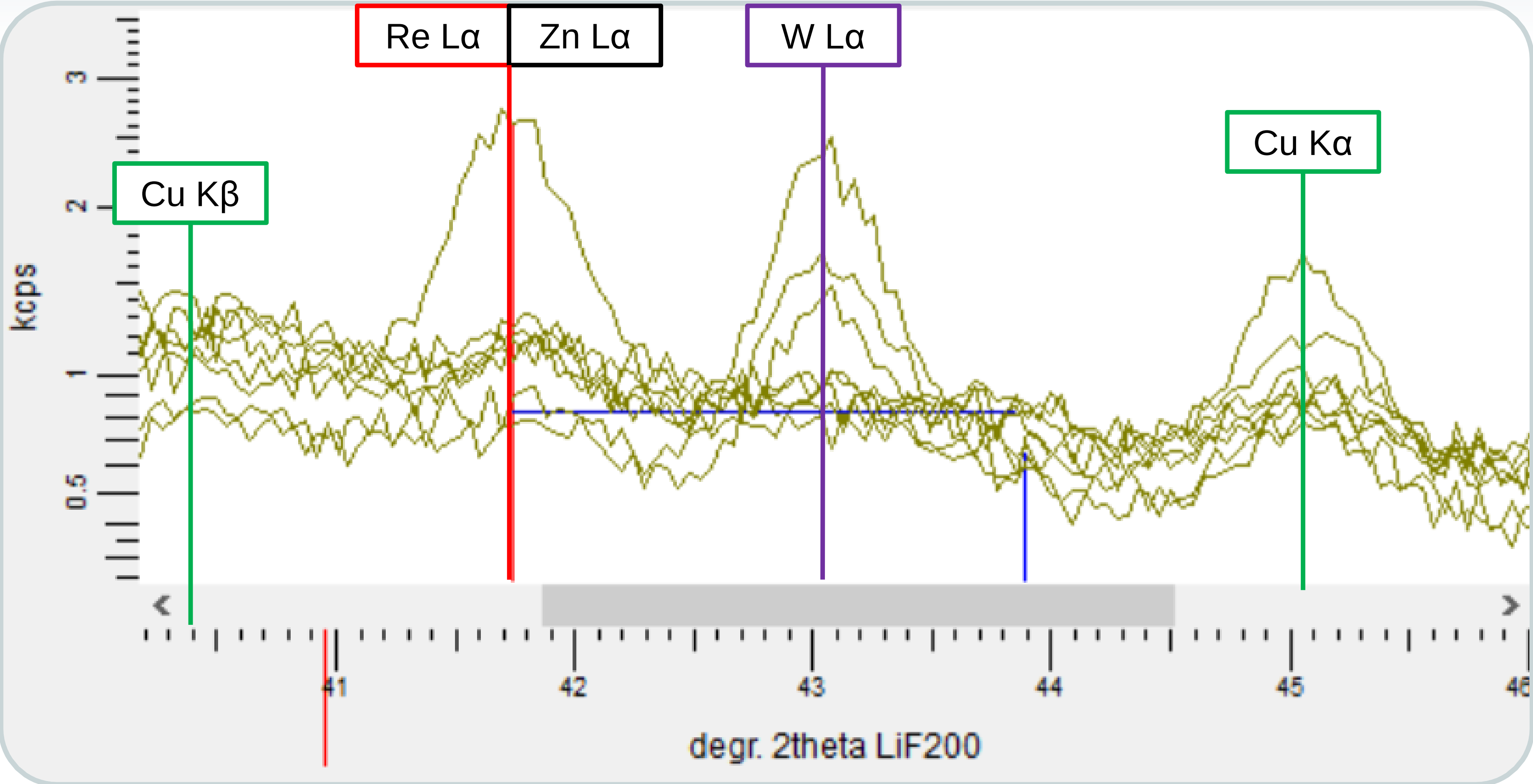
Blue S1, Black S2, Red S3

EDX Resolution Base on Silica Drift Detector

WDXRF Spectra – Pt LA
50kV / 100µm Al Filter / 0.23° / LiF 200



WDXRF Spectra – Re LA
50kV / 100µm Al Filter / 0.23° / LiF 200



Possible Overlaps in Slag

Element of Interest	Possible Overlapping Element
F Kα	Fe Lα & Fe Lβ
Na Kα	Zn Lα & Pd Lα Escape (EDXRF X-Ray Tube)
Mg Kα	
Al Kα	Br Lα
Si Kα	Sr Lα
P Kα	Zr Lα & Ca Kα Escape (EDXRF)
S Kα	Mo Lα
Cl Kα	Pd (Tube Line from EDXRF)
K Kα	Ca Kα

Element of Interest	Possible Overlapping Element
Ca Kα	
Ti Kα	Ba Lα Fe Kα Escape (EDXRF)
V Kα	Ti Kβ & Ce Lα
Cr Kα	V Kβ
Mn Kα	Cr Kβ
Fe Kα	Mn Kβ
Cu Kα	Ni Kβ
Zn Kα	Re Lα
Sr Kα	
Zr Kα	Sr Kβ
Pd Lα	Pd (EDXRF X-ray Tube) Rh (WDXRF X-Ray Tube)
Re Lα	Zn Kα & Cu Kβ
Re Lβ	
Pt Lα	Zn Lβ & W Lα (From Grinding Vessel / Sample)

Preparation

Slag Sample Preparation

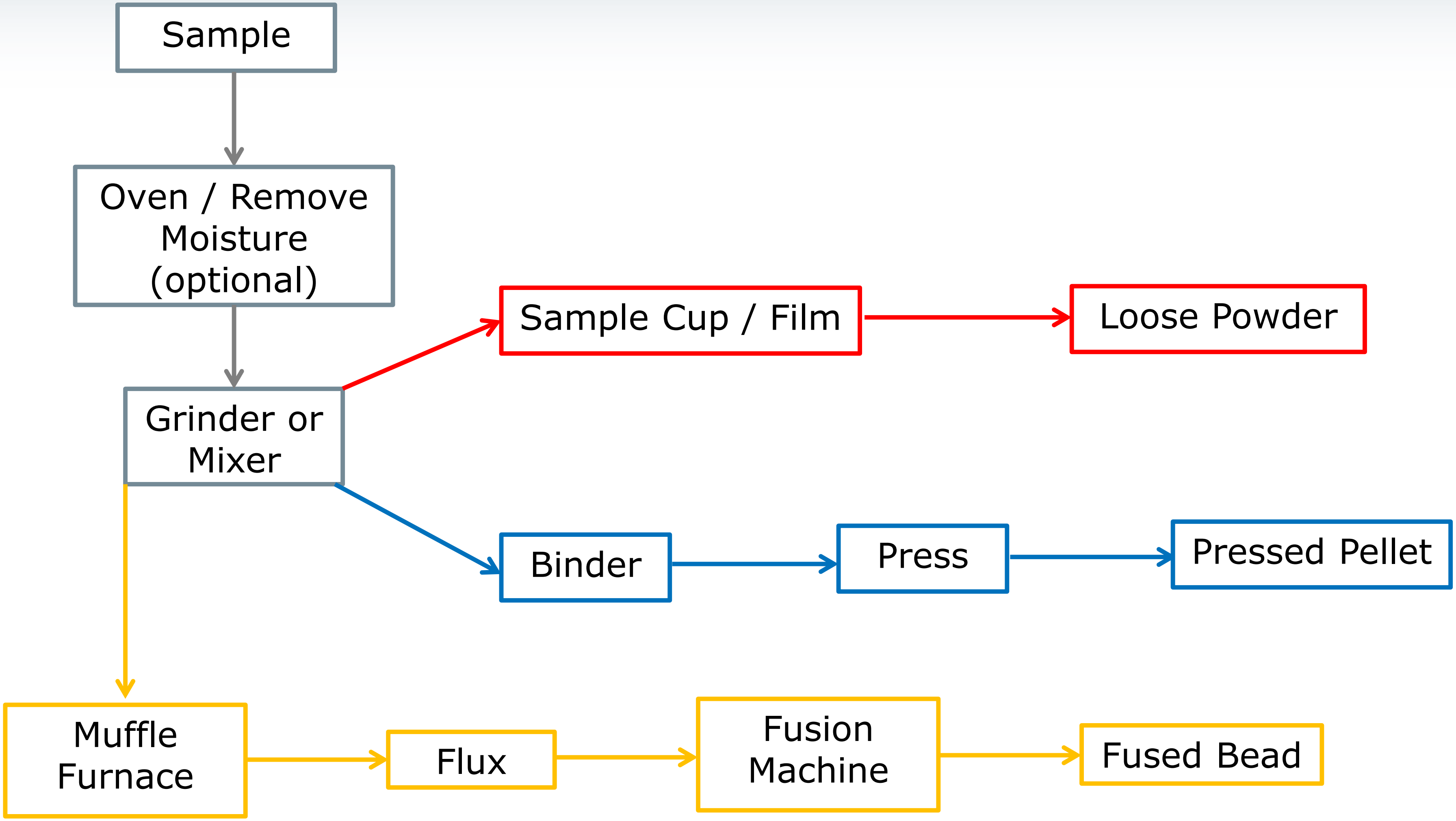
- Loose Powder
- Pressed Pellet
- Fused Bead

Loose Powder sample preparation for slag analysis is <u>not recommended</u>

Pressed Pellets is the <u>most practice sample preparation</u> technique for slag analysis in a steel plant

Fused Beads is <u>the best sample preparation technique</u> for slag analysis for a steel plant

Sample Preparation Flow Chart



Sample Preparation
Grinding the Sample

- Grinding can be done with:
  - Shatterbox / Ring & Puck
  - Mixer Mill

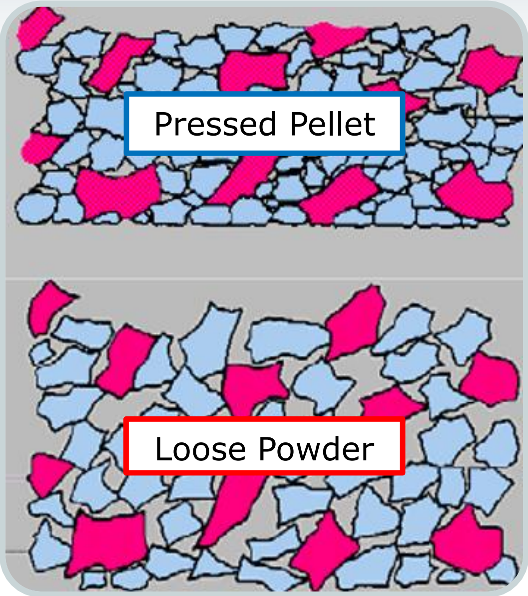
- Grind material to suitably small uniform particle size
  - Aids binding of material when pressing pellets
  - Aids dissolution when fusing samples
  - Allows several particle layers to be measured

Sample Preparation
Loose Powder

- Powder sample is placed into a sample cell with a suitable window and measured in helium
  - Prolene, Polypropylene, Mylar, Etnom, Kapton, etc…
- Issues with Loose Powder Samples:
  - Particles have air gaps between them
  - Arrangement of particles and air gaps is not reproducible

7.0g of Sample
Chemplex Cups PN 2143
40mm in Diameter
3.0µm Prolene Film

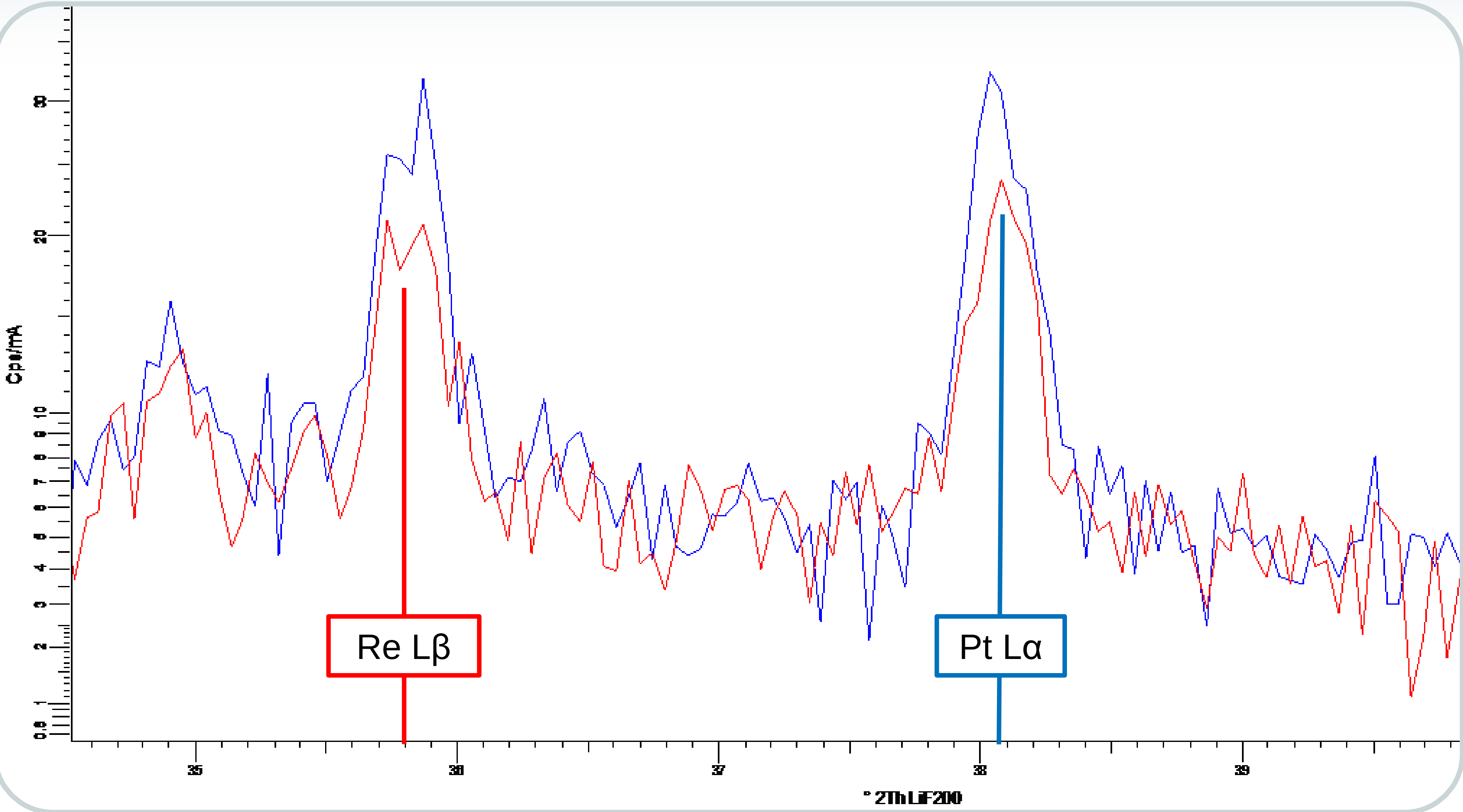
Sample Preparation
Pressed Pellet



- Powder is compacted under high pressure
- Typical pressure is 5 to 30 tons
- Typical holding time is 10 to 30 seconds
- Makes arrangement of particles and air gaps very reproducible
- Samples are typically pressed into Aluminum cups
- Provide support for samples
- Alternatively samples can be pressed onto a support material
  - Like Cellulose or Boric Acid
- Samples usually need the addition of binder to aid in forming a strong finished pellet

10.0g of Sample 1.0g of Wax Binder 40mm in Diameter	Grind Time = 30 Sec Press Time = 30 Sec Press Pressure = 30 T

Sample Preparation
Loose Powder Vs Pressed Pellet



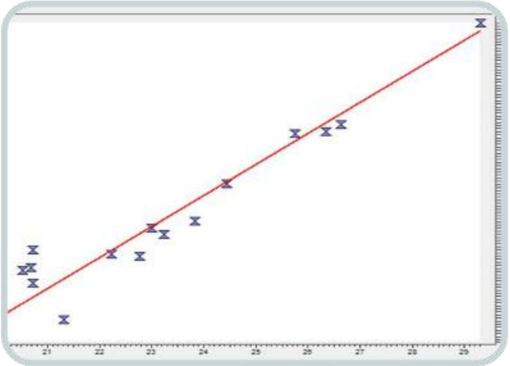
Sample Preparation
Fused Bead

- Small amount of sample is mixed with a large amount of flux and heated to around 1,000 ºC while being agitated
  - Common fluxes are Li2B4O7, LiBO2, or a combination of these two
  - Typical sample dilutions are from 1 part sample to 4 parts flux up to 1 part sample to 20 parts flux (or even higher)
  - Non-wetting agents like LiBr or LiI are normally added to ensure the molten sample does not stick to the crucible or the casting dish and to improve its flow characteristics
  - In some cases pre-oxidation of the sample must be done by adding an oxidizer like ammonium-nitrate and heating at a lower temperature before the actual fusion
- Preparation time is usually from 10 to 20 minutes

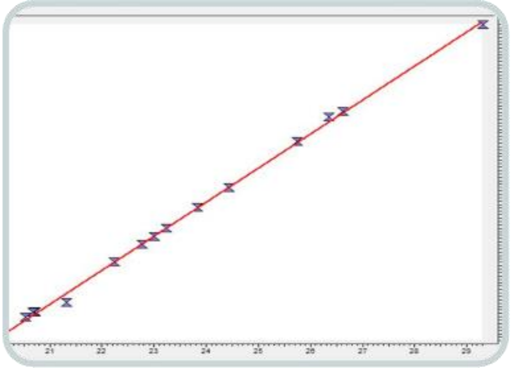
Sample Preparation
Fused Bead

SiO_2 Standards for Slag Calibration

Pressed Pellet Preparation



Fused Beads Preparation



- Removes Surface Roughness, Homogeneity Effects, & Particle Size Effects
- Removes mineralogical effect for highest accuracy by XRF
- Allows selection of unmatched standards
- Allows creation of synthetic standards

1.0000g of Sample 6.0000g of Flux 40mm in Diameter	49.75% LiT / 49.75% LiM / 0.5% LiBr (Wetting Agent) 2g of NH4NO3 (Oxidizer)

Sample Preparation (Pt)
WDXRF Loose Powder Vs Pressed Pellet

WDXRF - Loose Powder Precision Test (n=30) S2K5 - Pt (%)									
0.0193	0.0205	0.0206	0.0206	0.0201	0.0203	0.0223	0.0223	0.0219	0.0210
0.0217	0.0205	0.0209	0.0220	0.0212	0.0213	0.0211	0.0220	0.0230	0.0219
0.0229	0.0230	0.0221	0.0197	0.0218	0.0202	0.0235	0.0208	0.0248	0.0234
Average	**0.0215**	**Min**	**0.0193**	**Max**	**0.0248**	**Std Dev**	**0.0012**	**Rel Std Dev**	**5.6942**

WDXRF - Pressed Pellet Precision Test (n=30) S2K5 - Pt (%)									
0.0188	0.0185	0.0186	0.0184	0.0192	0.0190	0.0184	0.0183	0.0188	0.0187
0.0184	0.0183	0.0187	0.0185	0.0185	0.0182	0.0189	0.0189	0.0185	0.0195
0.0185	0.0182	0.0185	0.0186	0.0186	0.0187	0.0191	0.0184	0.0184	0.0195
Average	**0.0187**	**Min**	**0.0182**	**Max**	**0.0195**	**Std Dev**	**0.0003**	**Rel Std Dev**	**1.7927**

WDXRF - Loose Powder Precision Test (n=30) S3K3 - Pt (%)									
0.0064	0.0062	0.0050	0.0058	0.0052	0.0068	0.0053	0.0059	0.0044	0.0059
0.0056	0.0052	0.0071	0.0067	0.0067	0.0064	0.0068	0.0056	0.0048	0.0059
0.0060	0.0055	0.0061	0.0063	0.0049	0.0063	0.0058	0.0064	0.0058	0.0068
Average	**0.0059**	**Min**	**0.0044**	**Max**	**0.0071**	**Std Dev**	**0.0007**	**Rel Std Dev**	**11.2590**

WDXRF - Pressed Pellet Precision Test (n=30) S3K3 - Pt (%)									
0.0059	0.0060	0.0060	0.0058	0.0057	0.0056	0.0056	0.0056	0.0054	0.0059
0.0056	0.0055	0.0056	0.0057	0.0060	0.0060	0.0053	0.0055	0.0060	0.0054
0.0051	0.0057	0.0060	0.0057	0.0058	0.0057	0.0055	0.0058	0.0053	0.0057
Average	**0.0057**	**Min**	**0.0051**	**Max**	**0.0060**	**Std Dev**	**0.0002**	**Rel Std Dev**	**4.1513**

Sample Preparation (Pt)
EDXRF Loose Powder Vs Pressed Pellet

EDXRF - Loose Powder Precision Test (n=30) S2K5 - Pt (%)									
0.0189	0.0195	0.0138	0.0162	0.0220	0.0195	0.0210	0.0211	0.0269	0.0214
0.0243	0.0194	0.0178	0.0222	0.0144	0.0207	0.0224	0.0229	0.0215	0.0213
0.0183	0.0245	0.0223	0.0183	0.0153	0.0159	0.0283	0.0195	0.0287	0.0244
Average	0.0208	Min	0.0138	Max	0.0287	Std Dev	0.0037	Rel Std Dev	17.7254

EDXRF - Pressed Pellet Precision Test (n=30) S2K5 - Pt (%)									
0.0139	0.0145	0.0140	0.0143	0.0147	0.0142	0.0147	0.0144	0.0153	0.0130
0.0129	0.0152	0.0146	0.0154	0.0157	0.0153	0.0144	0.0141	0.0148	0.0137
0.0138	0.0141	0.0137	0.0139	0.0136	0.0146	0.0144	0.0139	0.0144	0.0148
Average	0.0143	Min	0.0129	Max	0.0157	Std Dev	0.0007	Rel Std Dev	4.5493

EDXRF - Loose Powder Precision Test (n=30) S3K3 - Pt (%)									
0.0119	0.0122	0.0105	0.0068	0.0096	0.0072	0.0093	0.0143	0.0108	0.0085
0.0072	0.0088	0.0079	0.0079	0.0075	0.0079	0.0089	0.0081	0.0107	0.0073
0.0085	0.0063	0.0084	0.0112	0.0136	0.0140	0.0085	0.0111	0.0073	0.0092
Average	0.0094	Min	0.0063	Max	0.0143	Std Dev	0.0022	Rel Std Dev	22.9420

EDXRF - Pressed Pellet Precision Test (n=30) S3K3 - Pt (%)									
0.0084	0.0078	0.0085	0.0090	0.0084	0.0077	0.0089	0.0081	0.0086	0.0081
0.0083	0.0074	0.0080	0.0093	0.0081	0.0085	0.0087	0.0069	0.0080	0.0070
0.0078	0.0074	0.0084	0.0084	0.0092	0.0091	0.0076	0.0080	0.0081	0.0076
Average	0.0082	Min	0.0069	Max	0.0093	Std Dev	0.0006	Rel Std Dev	7.3222

Sample Preparation (Pt)
Pressed Pellet WDXRF vs EDXRF

WDXRF - Pressed Pellet Precision Test (n=30) S2K5 - Pt (%)									
0.0188	0.0185	0.0186	0.0184	0.0192	0.0190	0.0184	0.0183	0.0188	0.0187
0.0184	0.0183	0.0187	0.0185	0.0185	0.0182	0.0189	0.0189	0.0185	0.0195
0.0185	0.0182	0.0185	0.0186	0.0186	0.0187	0.0191	0.0184	0.0184	0.0195
Average	**0.0187**	**Min**	**0.0182**	**Max**	**0.0195**	**Std Dev**	**0.0003**	**Rel Std Dev**	**1.7927**

EDXRF - Pressed Pellet Precision Test (n=30) S2K5 - Pt (%)									
0.0139	0.0145	0.0140	0.0143	0.0147	0.0142	0.0147	0.0144	0.0153	0.0130
0.0129	0.0152	0.0146	0.0154	0.0157	0.0153	0.0144	0.0141	0.0148	0.0137
0.0138	0.0141	0.0137	0.0139	0.0136	0.0146	0.0144	0.0139	0.0144	0.0148
Average	**0.0143**	**Min**	**0.0129**	**Max**	**0.0157**	**Std Dev**	**0.0007**	**Rel Std Dev**	**4.5493**

WDXRF - Pressed Pellet Precision Test (n=30) S3K3 - Pt (%)									
0.0059	0.0060	0.0060	0.0058	0.0057	0.0056	0.0056	0.0056	0.0054	0.0059
0.0056	0.0055	0.0056	0.0057	0.0060	0.0060	0.0053	0.0055	0.0060	0.0054
0.0051	0.0057	0.0060	0.0057	0.0058	0.0057	0.0055	0.0058	0.0053	0.0057
Average	**0.0057**	**Min**	**0.0051**	**Max**	**0.0060**	**Std Dev**	**0.0002**	**Rel Std Dev**	**4.1513**

EDXRF - Pressed Pellet Precision Test (n=30) S3K3 - Pt (%)									
0.0084	0.0078	0.0085	0.0090	0.0084	0.0077	0.0089	0.0081	0.0086	0.0081
0.0083	0.0074	0.0080	0.0093	0.0081	0.0085	0.0087	0.0069	0.0080	0.0070
0.0078	0.0074	0.0084	0.0084	0.0092	0.0091	0.0076	0.0080	0.0081	0.0076
Average	**0.0082**	**Min**	**0.0069**	**Max**	**0.0093**	**Std Dev**	**0.0006**	**Rel Std Dev**	**7.3222**

Sample Preparation (Pt)
Loose Powder WDXRF vs EDXRF

WDXRF - Loose Powder Precision Test (n=30) S2K5 - Pt (%)									
0.0193	0.0205	0.0206	0.0206	0.0201	0.0203	0.0223	0.0223	0.0219	0.0210
0.0217	0.0205	0.0209	0.0220	0.0212	0.0213	0.0211	0.0220	0.0230	0.0219
0.0229	0.0230	0.0221	0.0197	0.0218	0.0202	0.0235	0.0208	0.0248	0.0234
Average	**0.0215**	**Min**	**0.0193**	**Max**	**0.0248**	**Std Dev**	**0.0012**	**Rel Std Dev**	**5.6942**

EDXRF - Loose Powder Precision Test (n=30) S2K5 - Pt (%)									
0.0189	0.0195	0.0138	0.0162	0.0220	0.0195	0.0210	0.0211	0.0269	0.0214
0.0243	0.0194	0.0178	0.0222	0.0144	0.0207	0.0224	0.0229	0.0215	0.0213
0.0183	0.0245	0.0223	0.0183	0.0153	0.0159	0.0283	0.0195	0.0287	0.0244
Average	**0.0208**	**Min**	**0.0138**	**Max**	**0.0287**	**Std Dev**	**0.0037**	**Rel Std Dev**	**17.7254**

WDXRF - Loose Powder Precision Test (n=30) S3K3 - Pt (%)									
0.0064	0.0062	0.0050	0.0058	0.0052	0.0068	0.0053	0.0059	0.0044	0.0059
0.0056	0.0052	0.0071	0.0067	0.0067	0.0064	0.0068	0.0056	0.0048	0.0059
0.0060	0.0055	0.0061	0.0063	0.0049	0.0063	0.0058	0.0064	0.0058	0.0068
Average	**0.0059**	**Min**	**0.0044**	**Max**	**0.0071**	**Std Dev**	**0.0007**	**Rel Std Dev**	**11.2590**

EDXRF - Loose Powder Precision Test (n=30) S3K3 - Pt (%)									
0.0119	0.0122	0.0105	0.0068	0.0096	0.0072	0.0093	0.0143	0.0108	0.0085
0.0072	0.0088	0.0079	0.0079	0.0075	0.0079	0.0089	0.0081	0.0107	0.0073
0.0085	0.0063	0.0084	0.0112	0.0136	0.0140	0.0085	0.0111	0.0073	0.0092
Average	**0.0094**	**Min**	**0.0063**	**Max**	**0.0143**	**Std Dev**	**0.0022**	**Rel Std Dev**	**22.9420**

Sample Preparation (Pd)
Pressed Pellet – WDXRF

WDXRF – Pressed Pellet Precision Test (n=30) S3K3 - Pd (ppm)									
27.0	27.4	25.8	25.6	22.7	23.4	26.1	26.3	27.6	24.7
27.0	27.5	24.9	23.0	24.1	24.5	24.5	25.8	29.3	24.7
23.8	24.9	27.1	24.1	27.2	27.6	25.3	27.3	26.4	23.1
Average	**25.6**	**Min**	**22.7**	**Max**	**29.3**	**Std Dev**	**1.64**	**Rel Std Dev**	**6.40**

Qualitative, Quantitative & Semi-Quantitative Analysis

Qualitative, Quantitative, & Semi-Quantitative

Qualitative Analysis

- “What´s there ?“
- Used to identify the elements present in a specimen
- No reliable indication of the concentration levels present
- Can sometimes classify elements into major, minor or trace categories – BUT this can be risky

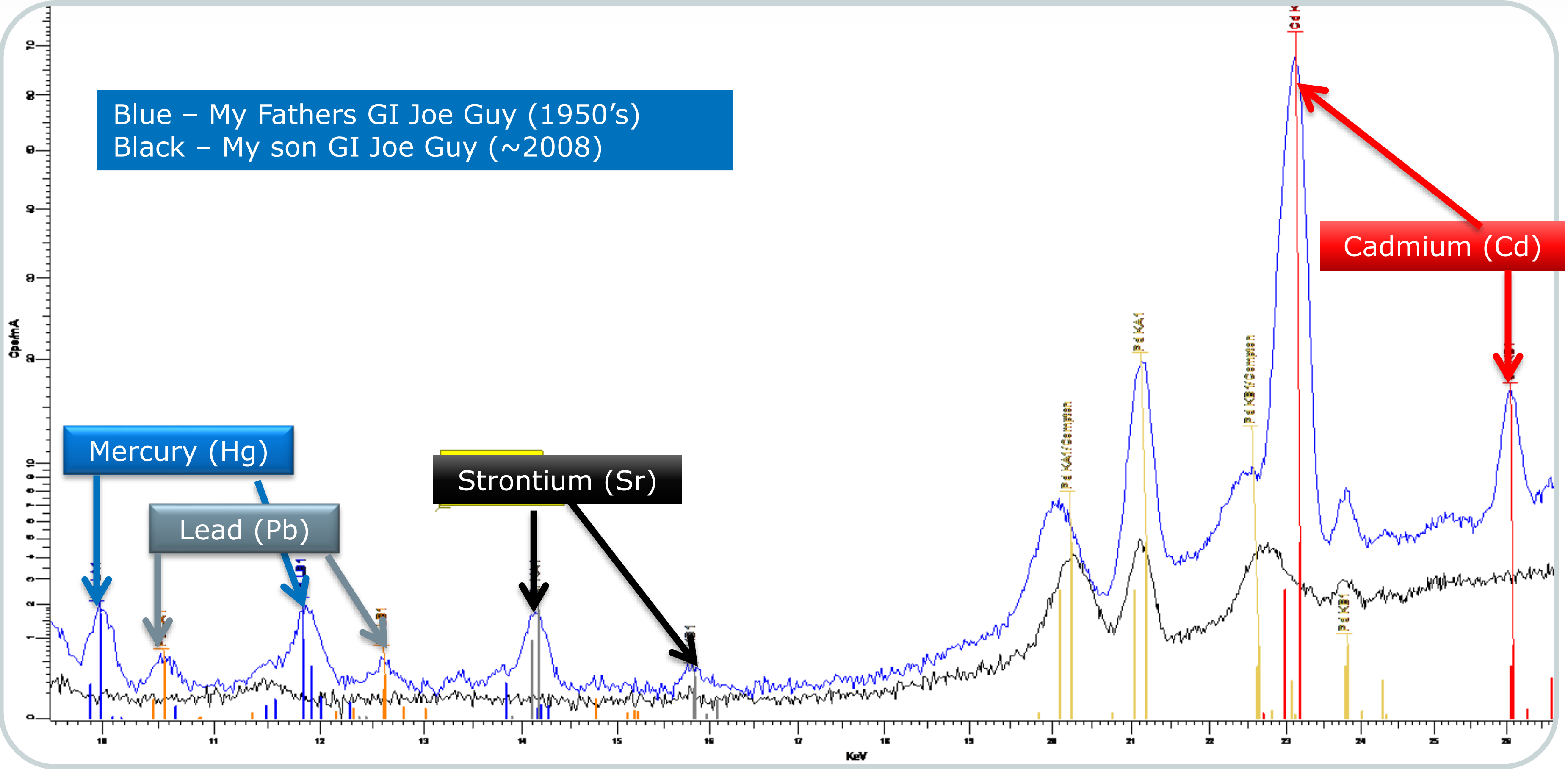
Quantitative Analysis

- “How much is there?“
- Used to determine sample composition
- Requires specific calibration standards and a time consuming calibration procedure
- Is justified for a large number of samples – Routine Analysis

Semi-Quantitative Analysis

- “About how much?“
- Bridges Qualitative and Quantitative Analysis
- “Nearly” as good as Quantitative
- Also refer to as Standardless

Example of Qualitative Analysis



Qualitative, Quantitative, & Semi-Quantitative

Qualitative Analysis

- “What´s there ?“
- Used to identify the elements present in a specimen
- No reliable indication of the concentration levels present
- Can sometimes classify elements into major, minor or trace categories – BUT this can be risky

Quantitative Analysis

- “How much is there?“
- Used to determine sample composition
- Requires specific calibration standards and a time consuming calibration procedure
- Is justified for a large number of samples – Routine Analysis

Semi-Quantitative Analysis

- “About how much?“
- Bridges Qualitative and Quantitative Analysis
- “Nearly” as good as Quantitative
- Also refer to as Standardless

Requirements for Selecting Calibration Standards (1)

- Contains all of the elements that you need to report. Additionally other elements may need to be measured even if they do not need to be reported if:
  - There is an element that is overlapping with the element of interest
  - There are elements that may have a large absorption or enhancement influence on the element of interest

- Unknown samples should be within the calibrated concentration range
  - Linear up to 10% from your lowest and highest concentration, anything past this will give inaccurate results

- Should be close to the same particle/grain size of your unknown samples (For Loose Powder and Pressed Pellets)
  - EXTREMELY important for low energy lines (F, Na_2O, MgO, Al_2O_3, etc…) where the penetration depth is small

- Total sum of each standard should be close to 100%, which will allow the use of Theoretical Corrections

Requirements for Selecting Calibration Standards (2)

- Different Material need different standards (except for fused beads)
  - EAF Slag ≠ LMF Slag ≠ BOF Slag
  - Limestone ≠ Sand ≠ Clay
- Standards should be prepared the same way as your unknowns
  - Cannot run Pressed Pellets against a Loose Powder Calibration
  - Cannot run Loose Powders against a Pressed Pellet Calibration
- If certified reference materials cannot be found or only a few can be found / purchased then it is acceptable to use "Secondary" Standard
- Make sure all standard values are entered in the correct form:
  - Fe / FeO / Fe2O3
  - S / SO3

"Secondary Standards"

- Take "100g" of sample and send "10g" to be analyzed by a testing facility / outside lab
  - Have them run the sample(s) using Fire Assay, ICP, AA, WDXRF, etc….
  - The report values from the testing lab will be used as the "certified" value of the remaining "90g"

"Secondary" Standards help with:

- Reporting missing elements not in certified standards
- Difference in particle size between certified and unknown samples
- Helps with mineralogical effect
- Extending the calibration range

- Recommendation is to mix and match certified standards with secondary standards

Number of Standards Required

Recommended number of standards to define a calibration:

- n = 3 X k (each calibrated line stands on its own)

Where:

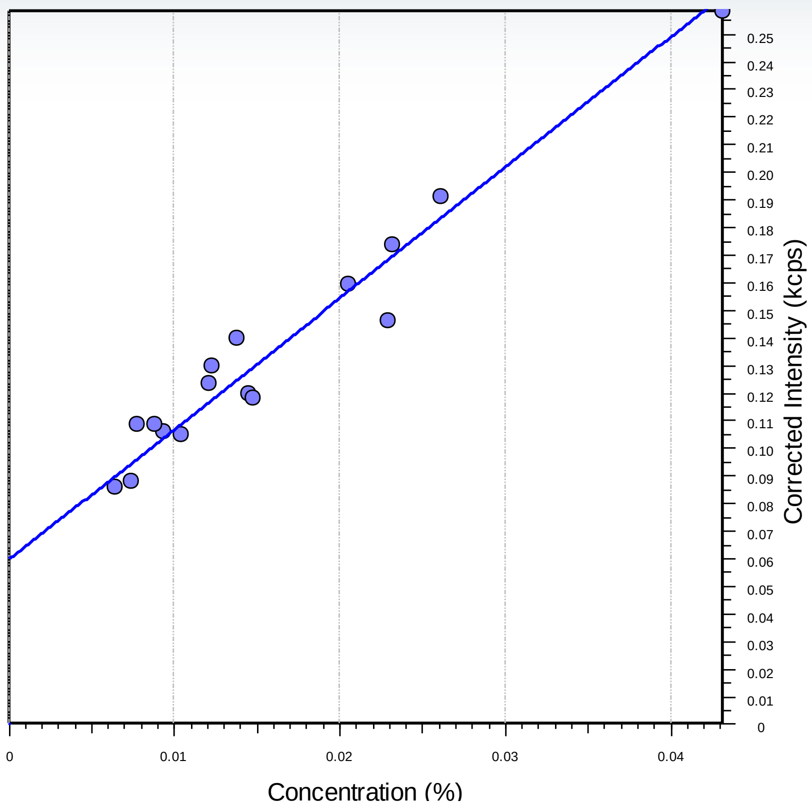
- n = minimum number of standards
- k = the number of calculated (Empirical) corrections
    - Calibration Line Slope
    - Calibration Line Offset
    - Line Overlap correction
    - Empirical Matrix correction
    - Quadratic correction
  - Standards with very similar concentrations only count as one

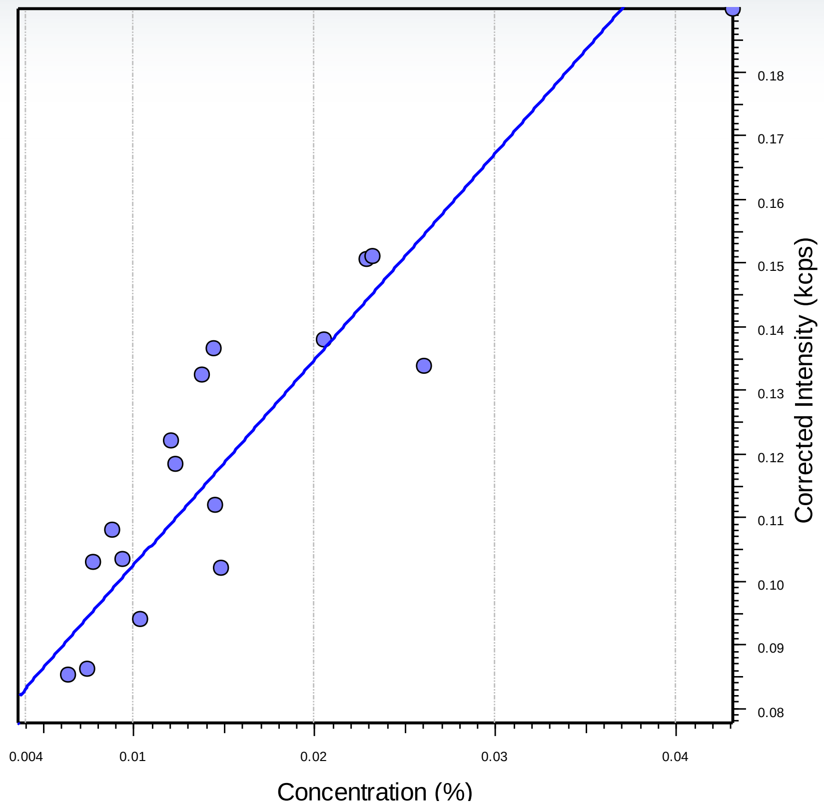
Calibration Standards for Precious Metals in Slag

- Main Elements of Interest: Pd, Pt, Re

- 17 "secondary" standards were provided
  - Pd and Pt results were from Fire Assay
    - 5 standards contain Pd
    - 17 standards contained Pt
    - 10 standards contained Re
  - All other elements results came from a "standardless" program
- Additional 20 Certified Standards NH 141 – NH 156 (EAF) and 7-1-005 – 7-1-015 (LMF) included to make calibration more reliable.

Calibration for Platinum LA WDXRF (65 – 431 ppm)

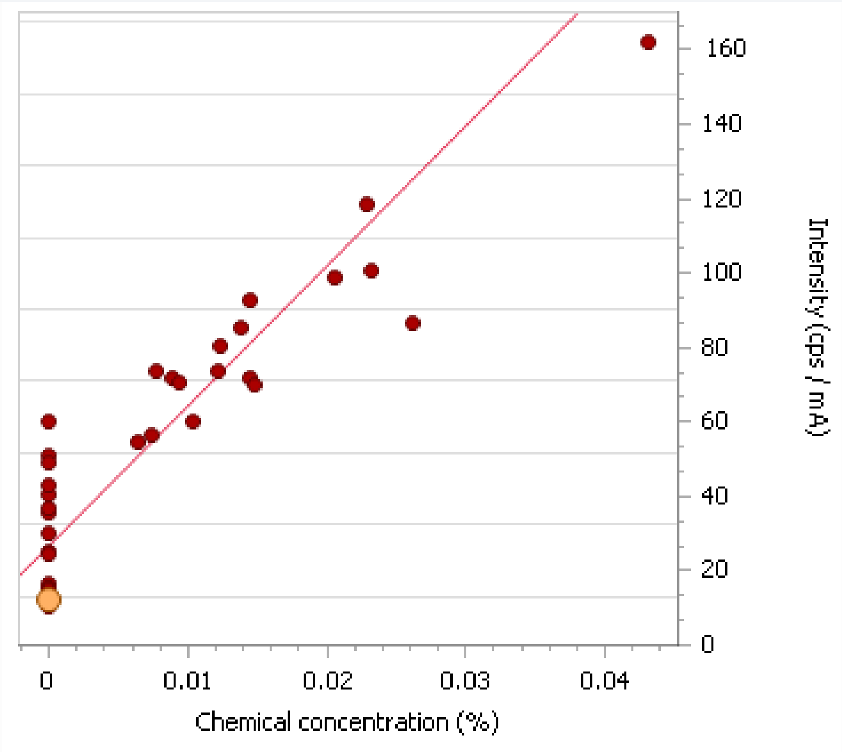


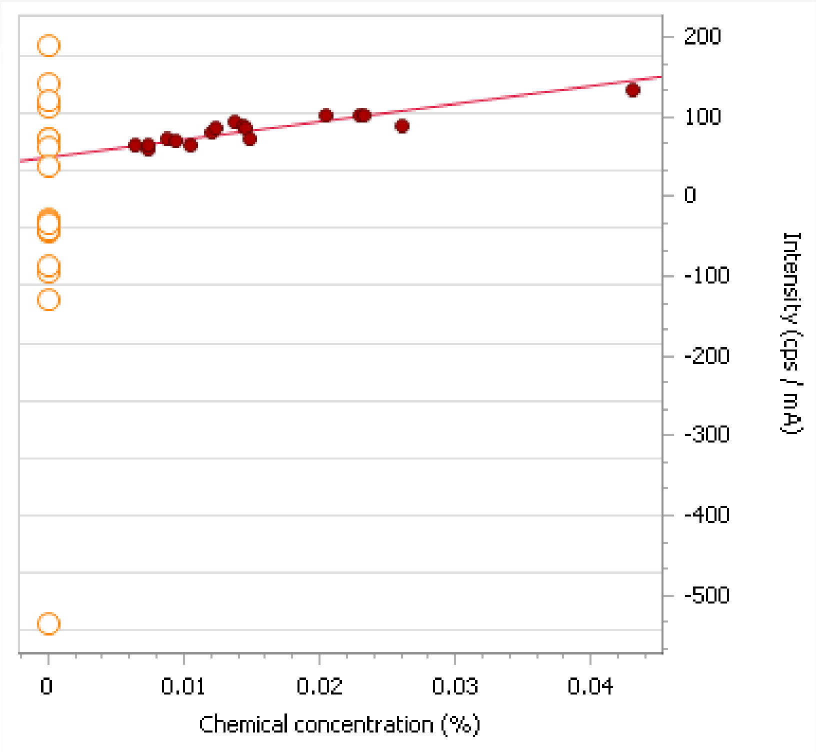


Pressed Pellet
Std Dev = 21 ppm
R2 = 0.950890
LLD = 5 ppm

Loose Powder
Std Dev = 32 ppm
R2 = 0.826828
LLD = 8 ppm

Calibration for Platinum **LA** EDXRF (65 – 431 ppm)

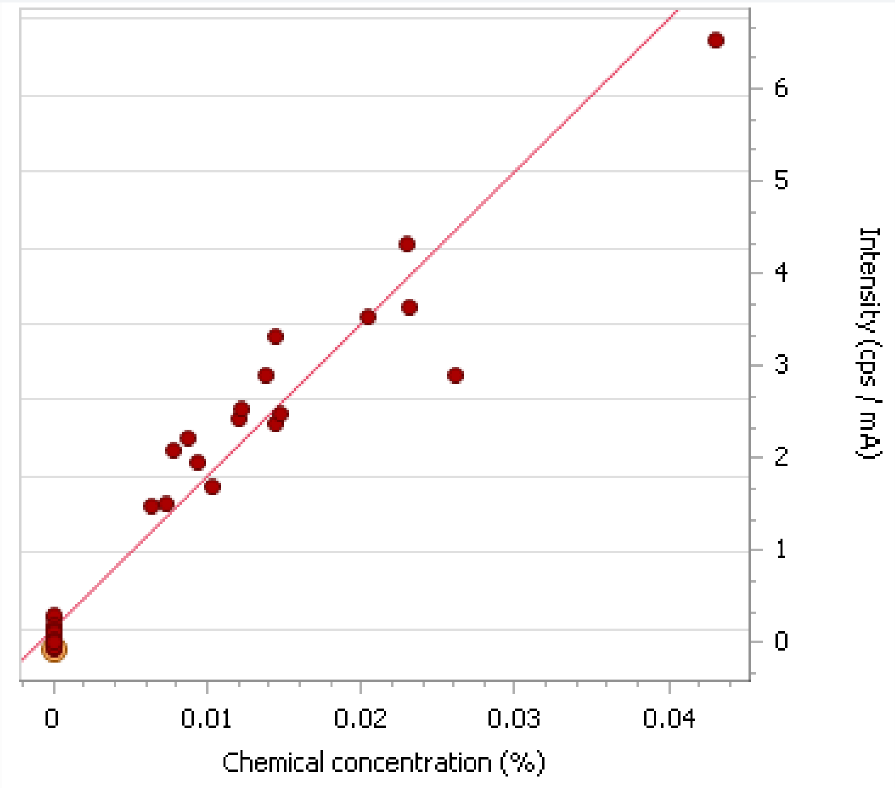


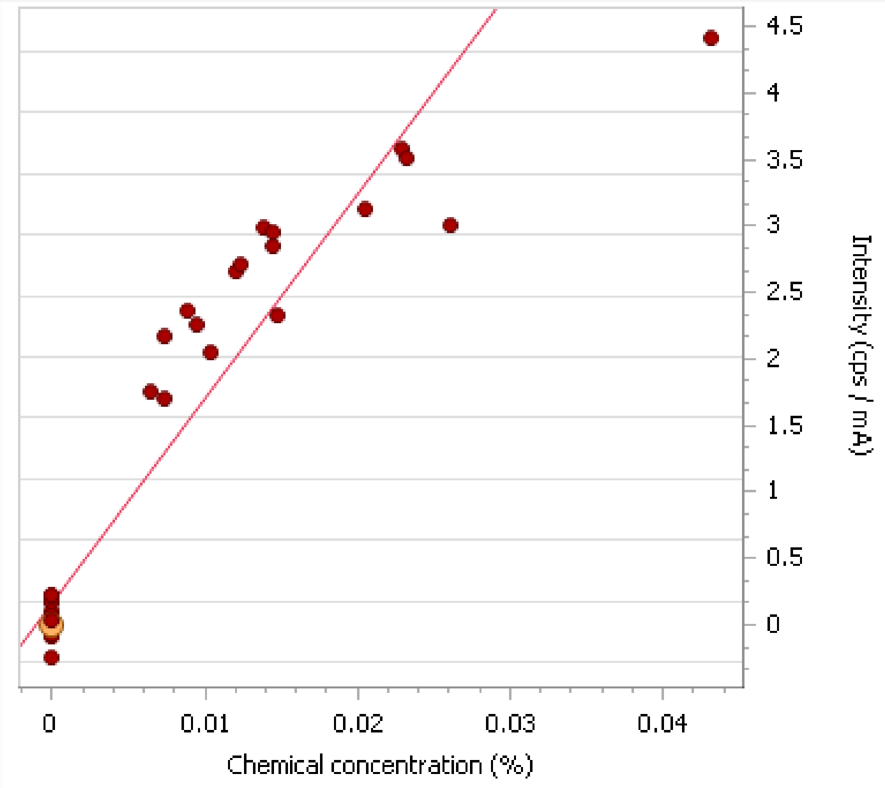


Pressed Pellet
Std Dev = 40 ppm
R2 = 0.84506
LLD = 3 ppm

Loose Powder
Std Dev = 37 ppm
R2 = 0.83792
LLD = 7 ppm

Calibration for Platinum **LB2,15** EDXRF (65 – 431 ppm)





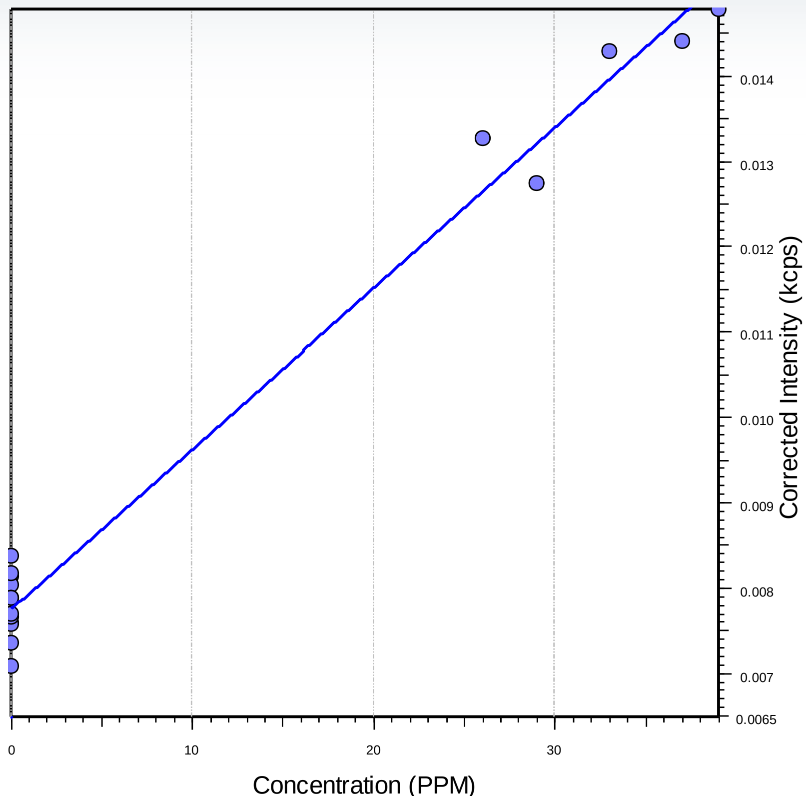
Pressed Pellet
Std Dev = 25 ppm
R2 = 0.94167
LLD = 14 ppm

Loose Powder
Std Dev = 39 ppm
R2 = 0.85568
LLD = 16 ppm

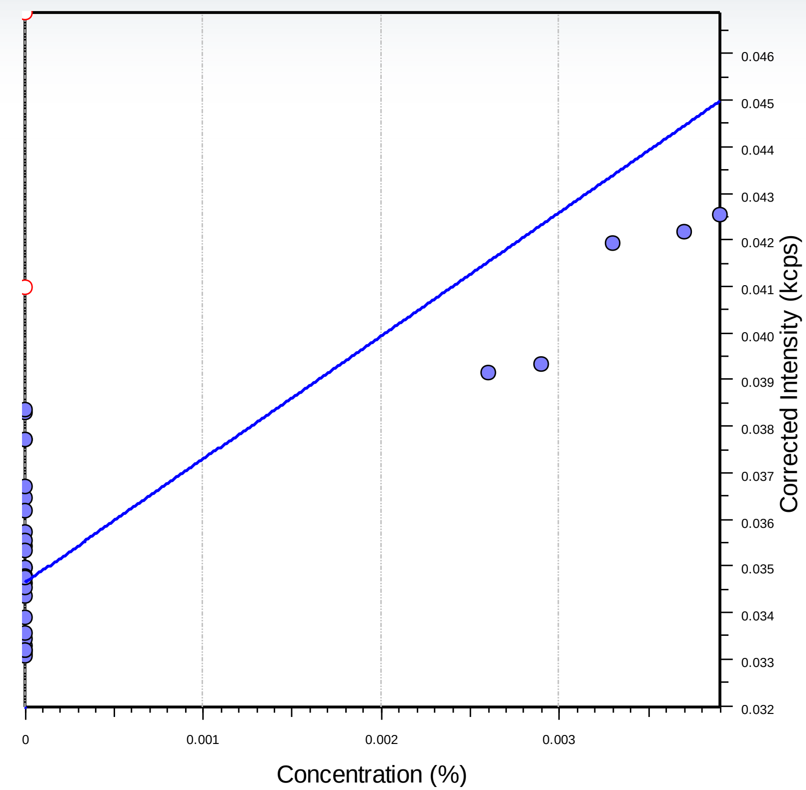
Standards Ran as Unknowns WDXRF - Platinum

Name	Pt(%)	WDXRF PP	WDXRF LP	EDXRF PP	EDXRF LP
S1-K1	0.0104	0.0094	0.0058	0.0097	0.0061
S1-K2	0.0148	0.0120	0.0072	0.0139	0.0067
S1-K3	0.0138	0.0165	0.0165	0.0168	0.0170
S1-K4	0.0145	0.0123	0.0109	0.0136	0.0165
S1-K5	0.0123	0.0153	0.0156	0.0166	0.0204
S1-K6	0.0205	0.0209	0.0179	0.0210	0.0177
S1-K7	0.0431	0.0417	0.0322	0.0384	0.0338
S2-K1	0.0144	0.0215	0.0229	0.0193	0.0143
S2-K2	0.0121			0.0135	0.0105
S2-K3	0.0232	0.0285	0.0338	0.0292	0.0434
S2-K4	0.0261	0.0274	0.0173	0.0166	0.0135
S2-K5	0.0229	0.0186	0.0229	0.0246	0.0163
S3-K1	0.0088	0.0102	0.0142	0.0115	0.0178
S3-K2	0.0094	0.0092	0.0128	0.0098	0.0200
S3-K3	0.0074	0.0054	0.0070	0.0075	0.0097
S3-K4	0.0078	0.0096	0.0121	0.0103	0.0154
S3-K5	0.0064	0.0047	0.0065	0.0069	0.0094

Calibration for Palladium WDXRF (0 – 39 ppm)

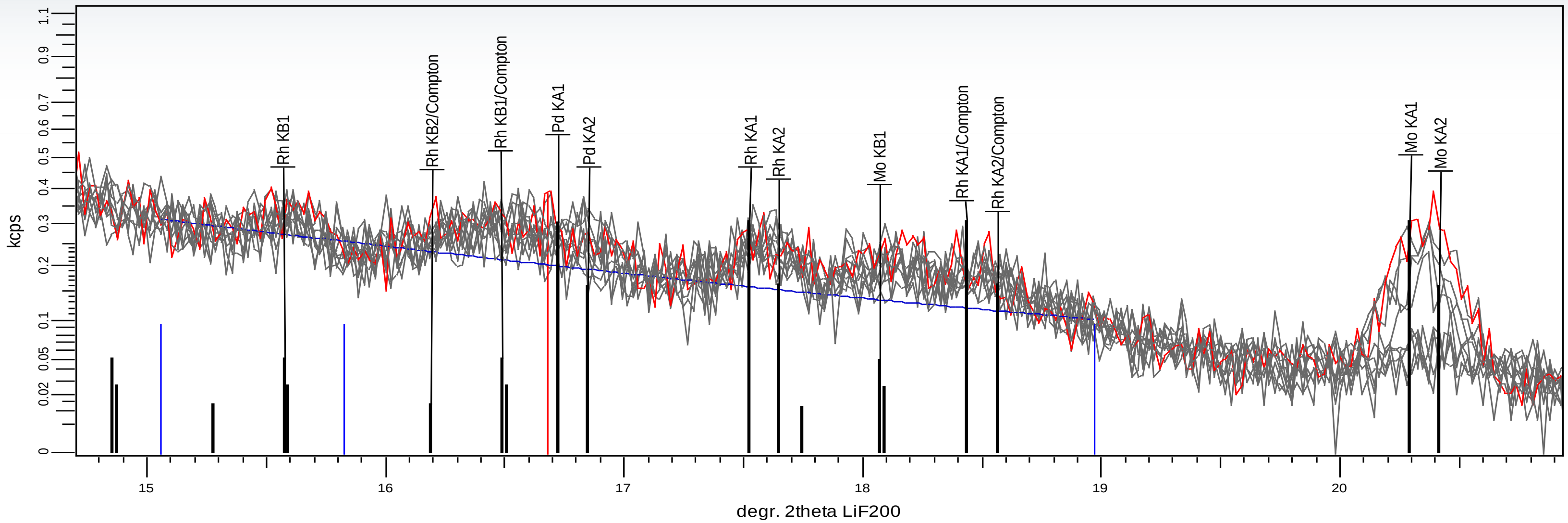


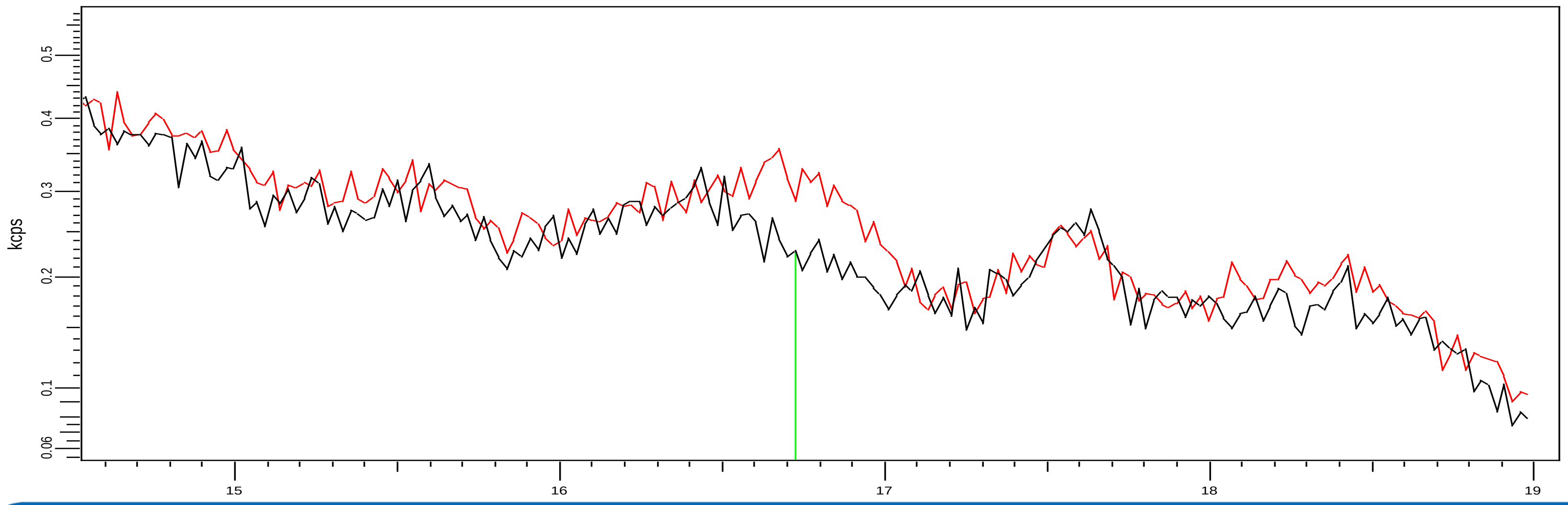
Pressed Pellet
Std Dev = 2 ppm
R2 = 0.982726
LLD = 1.8 ppm



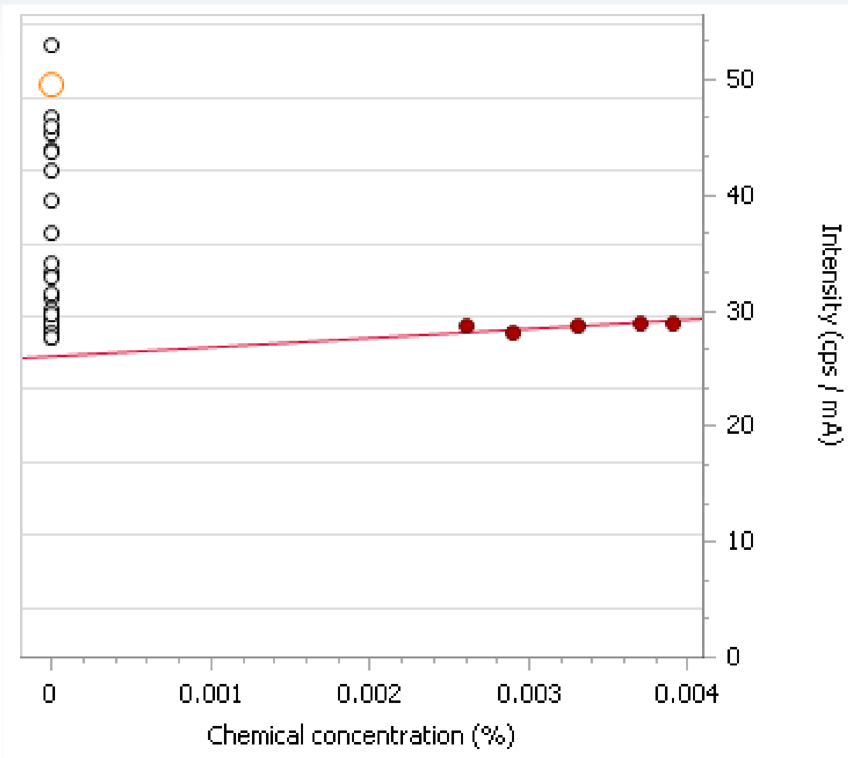
Loose Powder
Std Dev = 7 ppm
R2 = 0.692051
LLD = 6 ppm

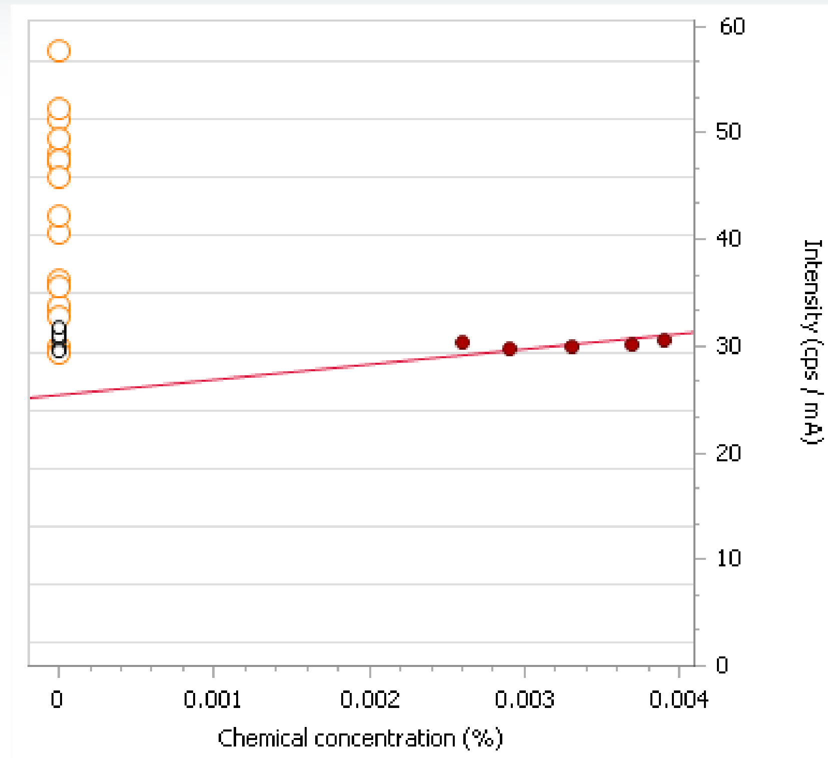
Palladium WDXRF Scans





Calibration for Palladium EDXRF (0 – 39 ppm)

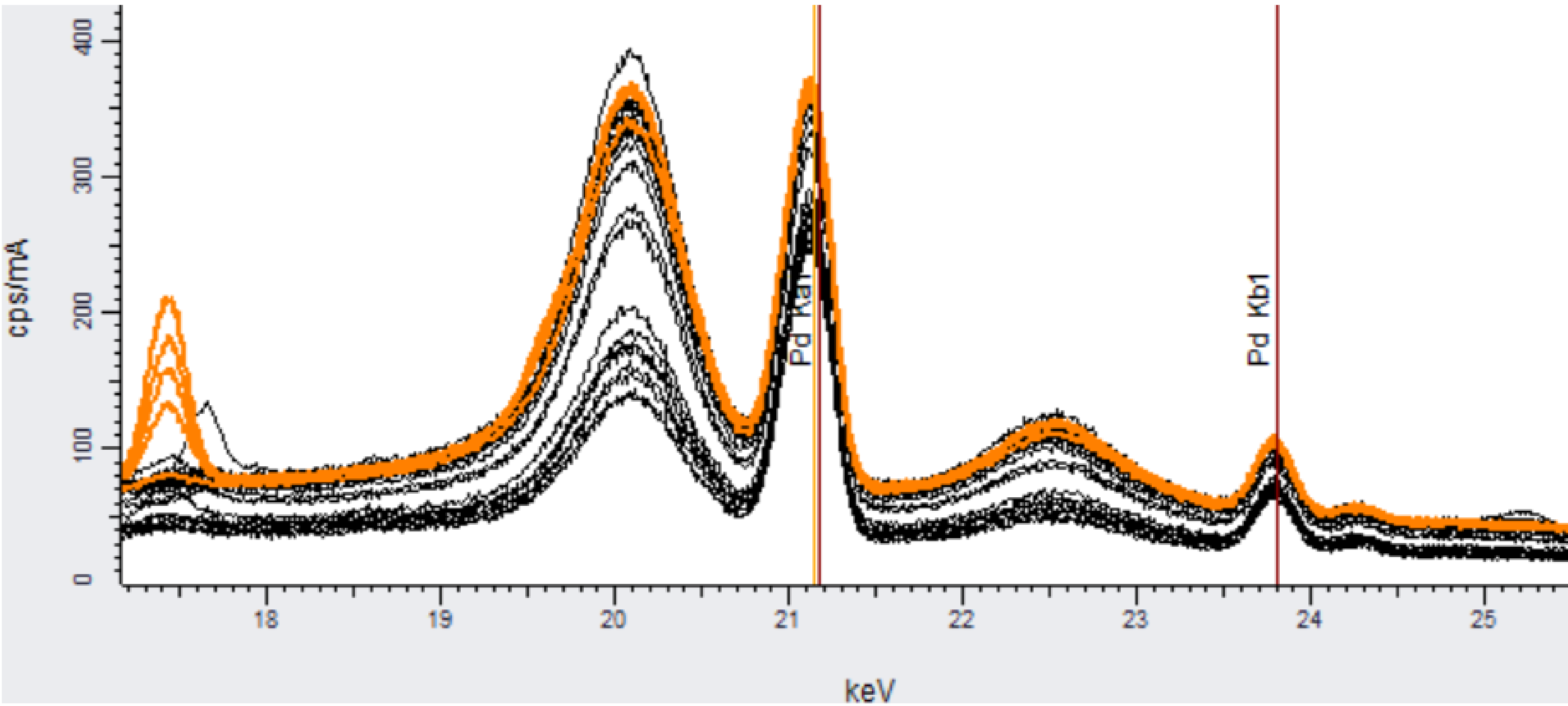




Pressed Pellet
Std Dev = 4 ppm
R2 = 0.52160
LLD = 8 ppm

Loose Powder
Std Dev = 5 ppm
R2 = 0.18517
LLD = 2 ppm

Palladium EDXRF Scans



Standards Ran as Unknowns WDXRF - Palladium

Name	Pd(%)	WDXRF PP	WDXRF LP	EDXRF PP	EDXRF LP
S1-K1	T	0.0000	0.0011	0.0083	0.0014
S1-K2	T	0.0000	0.0015	0.0050	0.0000
S1-K3	T	0.0000	0.0013	0.0074	0.0018
S1-K4	T	0.0000	0.0013	0.0066	0.0038
S1-K5	T	0.0000	0.0012	0.0164	0.0106
S1-K6	T	0.0000	0.0013	0.0074	0.0010
S1-K7	T	0.0000	0.0012	0.0054	0.0029
S2-K1	T	0.0004	0.0012	0.0044	0.0048
S2-K2	T	0.0000		0.0041	0.0000
S2-K3	T	0.0006	0.0023	0.0327	0.0221
S2-K4	T	0.0000	0.0013	0.0033	0.0000
S2-K5	T	0.0000	0.0012	0.0011	0.0000
S3-K1	0.0039	0.0035	0.0039	0.0001	0.0124
S3-K2	0.0037	0.0031	0.0036	0.0000	0.0176
S3-K3	0.0029	0.0027	0.0028	0.0000	0.0148
S3-K4	0.0033	0.0033	0.0036	0.0000	0.0123
S3-K5	0.0026	0.0025	0.0026	0.0000	0.0133

Unknown Samples

- Results should <u>NOT</u> be Normalized
- Total Sum should be between 96 – 102 %
- What if the Slags are Reading lower than 96% or Higher than 102%?
  - Broken Sample (covering tube / detector)
  - Sample Preparation Error
  - Requires Drift Correction
  - Incorrect Corrections being applied to the calibration
  - Outside Calibration Range

Qualitative, Quantitative, & Semi-Quantitative

Qualitative Analysis

- “What´s there ?“
- Used to identify the elements present in a specimen
- No reliable indication of the concentration levels present
- Can sometimes classify elements into major, minor or trace categories – BUT this can be risky

Quantitative Analysis

- “How much is there?“
- Used to determine sample composition
- Requires specific calibration standards and a time consuming calibration procedure
- Is justified for a large number of samples – Routine Analysis

Semi-Quantitative Analysis

- “About how much?“
- Bridges Qualitative and Quantitative Analysis
- “Nearly” as good as Quantitative
- Also refer to as Standardless

Standardless Analysis
What does "Nearly" as good mean?

Typical accuracies

- Depend on sample type and are generally not predictable
- Within 5-20% of true value for Majors (> 10 wt-%)
- Within 10-30% of true value for Minors (0.1 - 10 wt-%)
- Usually within 20-300% of true value for Traces (< 0.1 wt-%)

Guidelines for Standardless Analysis

- Run some “Certified” Standards as “Unknowns” with the standardless program to get feel of accuracy.

- The better the sample preparation the better the results.
  - Flat Solids Samples, Press Pellets, Liquids, Fused Bead, etc….

- After “new” samples are ran, do not report the results until the data is reviewed and if needed recalculated
  - View the spectra and remove any elements not presents
  - Verify peak is actually that element and not KB, LB, overlap of another element

- Usually the more you “tell” the Standardless program the better the results will be:
  - LOI
  - Matrix is H_2O, CH_2, etc…
  - CaO or $CaCO_3$, S or SO_3, etc…

- Be careful in reporting traces <100ppm

- If you use standardless routinely for the same sample then make a custom made standardless program like $CaCO_3$ Matrix, Bag House Dust, etc…

Platinum “Standardless” Results

Name	Pt(%)	WDXRF PP	WDXRF LP	EDXRF PP	EDXRF LP
S1-K1	0.0104	0.0086	0.0087	0.0056	0.0070
S1-K2	0.0148	0.0109	0.0085	0.0068	0.0077
S1-K3	0.0138	0.0105	0.0109	0.0090	0.0111
S1-K4	0.0145	0.0079	0.0102	0.0070	0.0072
S1-K5	0.0123	0.0098	0.0129	0.0082	0.0106
S1-K6	0.0205	0.0129	0.0136	0.0112	0.0101
S1-K7	0.0431	0.0229	0.0180	0.0213	0.0157
S2-K1	0.0144	0.0156	0.0139	0.0126	0.0126
S2-K2	0.0121	0.0127	0.0132	0.0089	0.0104
S2-K3	0.0232	0.0176	0.0157	0.0153	0.0139
S2-K4	0.0261	0.0135	0.0138	0.0116	0.0115
S2-K5	0.0229	0.0168	0.0149	0.0167	0.0137
S3-K1	0.0088	0.0110			
S3-K2	0.0094	0.0083			
S3-K3	0.0074	0.0088			
S3-K4	0.0078	0.0074			
S3-K5	0.0064	0.0078			

Palladium "Standardless" Results

Name	Pd(%)	WDXRF PP	WDXRF LP	EDXRF PP	EDXRF LP
S1-K1	T	0.0000	0.0000	0.0025	0.0023
S1-K2	T	0.0000	0.0000	0.0024	0.0024
S1-K3	T	0.0000	0.0000	0.0025	0.0024
S1-K4	T	0.0000	0.0000	0.0025	0.0023
S1-K5	T	0.0000	0.0000	0.0025	0.0026
S1-K6	T	0.0000	0.0000	0.0025	0.0024
S1-K7	T	0.0000	0.0000	0.0025	0.0023
S2-K1	T	0.0000	0.0000	0.0025	0.0025
S2-K2	T	0.0000	0.0000	0.0025	0.0022
S2-K3	T	0.0000	0.0000	0.0028	0.0028
S2-K4	T	0.0000	0.0000	0.0024	0.0022
S2-K5	T	0.0000	0.0000	0.0024	0.0230
S3-K1	0.0039	0.0081			
S3-K2	0.0037	0.0075			
S3-K3	0.0029	0.0063			
S3-K4	0.0033	0.0081			
S3-K5	0.0026	0.0052			

Conclusion

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Innovation with Integrity

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