Analytical Options for the Determination of Platinum and Ruthenium in Complex Matrices

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Assay Considerations

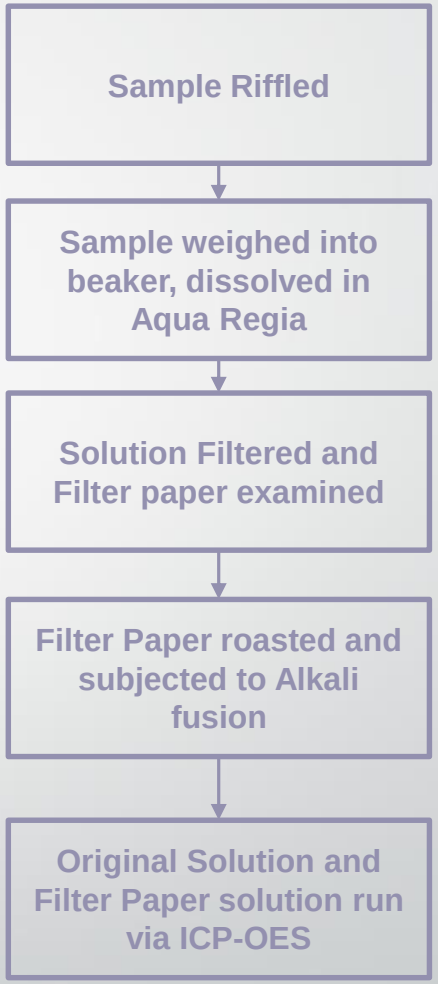
- X-Ray Fluorescence
- Direct Acid Leach
- Pb collection Fire Assay
- Alkali Fusion
- NiS Fire Assay
- Distillation

X-Ray Fluorescence Analysis

- Major elements
  - Ru, Cl, Pt, Co, Nb, Cr, Ta, Si, Al, Fe, Mo, Ti, W
- Minor elements
  - Ni, S, Ag, Re, Pd, Ca, Rh

Direct Acid Leach

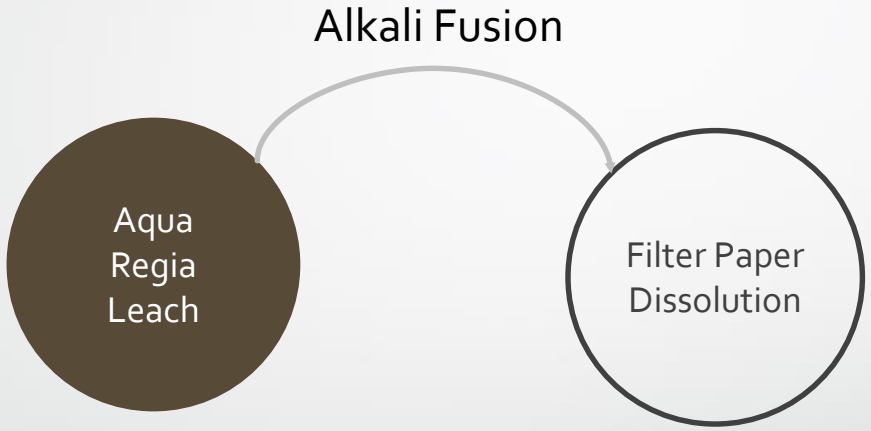
- Insoluble Ru disrupts dissolution of Pt
- Requires residue to be put in solution via alternative method
- Many samples resistant to direct acid attack



Direct Acid Residue

- Filter Papers after initial dissolve in Aqua Regia
- Black residue presumed to be undissolved Ru as well as Pt

Direct Acid Leach Results



Rep-1 : Pt 4.881%
Rep-2 : Pt 4.886%

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Rep-1 FP: Pt 6.583%
Rep-2 FP: Pt 6.507%

Rep-1 : Pt 11.464% Ru 40.63%
Rep-2 : Pt 11.393% Ru 39.95%

Pb Collection Fire Assay

- Ruthenium lost
- Proper flux selection crucial
- Expensive

Sample Riffled

Sample Weighed with appropriate flux and fused

Fusion Pb buttons separated and cupelled to recover Pt containing Ag beads

Beads dissolved in Aqua Regia, AgCl precipitated and filtered

Filter paper containing AgCl and trace Pt re-fused, cupelled

Bead dissolved in Aqua Regia, filtered in to volumetric

Solution run via ICP-OES

Sample Size Study

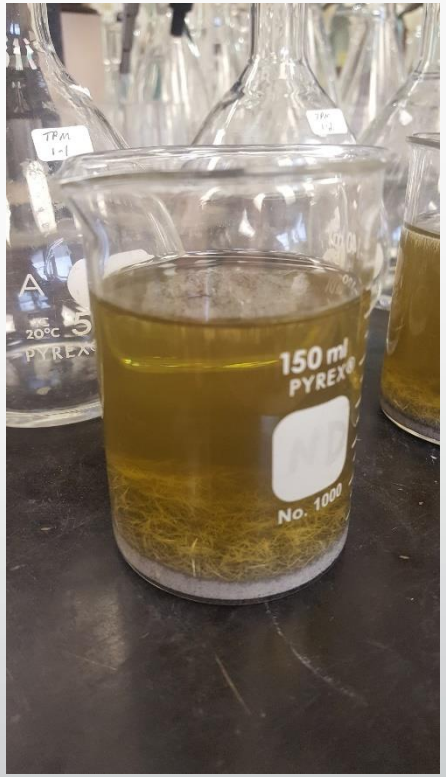
- Pb Collection Fire Assay
- 4 different sample sizes
- 1g, 0.75, 0.5, and 0.25
- Ru visible on Ag bead

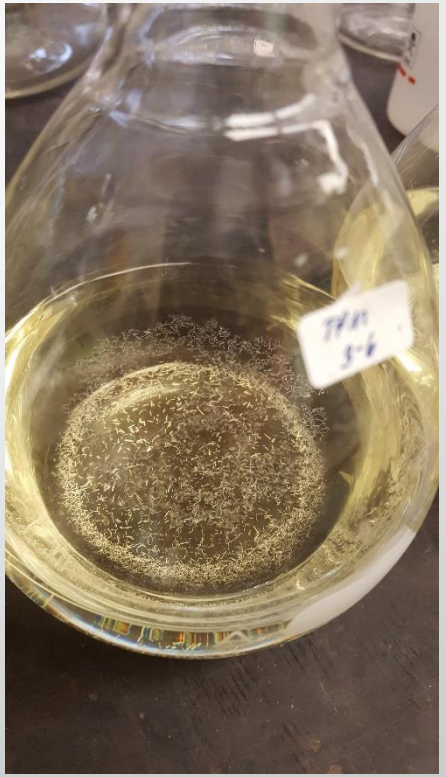
Sample Size Study

- Ruthenium and/or PGMs present on Ag collection beads

Pb present after Fire Assay

- Normally, cupellation process separates Pb from precious metals
- High Ru samples retain more Pb and PGMs through cupellation
- Concentration is high enough it will form crystals even after filtration (concentration ~800ppm)





Sample Size Results

- Best replicates sample sizes 0.50g and 0.75g
- Lowest RSD values

Sample Size (g)	%Pt	RSD
1.00	11.65	0.36%
0.75	11.63	0.08%
0.50	11.61	0.11%
0.25	11.53	0.55%

Why the mid range samples?

- Higher sample sizes create problems in the Fire Assay fusion
- Low sample sizes can create non-representative replicates when riffling
- Mid range sample weights split the difference, yield the most consistent results

Sample Size (g)	%Pt	RSD
1.00	11.65	0.36%
0.75	11.63	0.08%
0.50	11.61	0.11%
0.25	11.53	0.55%

Varying Techniques for ICP-OES

- Samples contain high concentration of Pb (~800ppm)

- Options

1. Dilute the sample until the Pb is low enough not to interfere
2. Attempt to run the sample as is with the elevated Pb concentration
3. Create matrix matched, high Pb Standards to calibrate with

Option 1

- Dilute the sample until the Pb is low enough not to interfere
- 10X dilution made, dropping Pb concentration to ~80ppm

Sample Size (g)	%Pt	RSD
1.00	11.65	0.36%
0.75	11.63	0.08%
0.50	11.61	0.11%
0.25	11.53	0.55%

Option 2

- Attempt to run the sample as is, with the elevated Pb concentration
- Pb is ~800ppm

Sample Size (g)	%Pt	RSD
1.0	11.85	0.82%
0.75	11.62	1.61%
0.5	11.69	0.85%
0.25	11.72	0.74%

Option 3

- Create matrix matched, high Pb Standards to calibrate with
- Standards match samples with 800ppm Pb present

Sample Size (g)	%Pt	RSD
1.00	11.77	2.10%
0.75	12.41	4.99%
0.50	12.03	2.98%
0.25	12.23	4.55%

Three Techniques, side by side

Results for Sample size 0.50g

Run type	%Pt	RSD
Diluted 10x	11.61	0.11%
Ran as is, Pb 800 ppm	11.69	0.85%
High Pb standards	12.03	2.98%

Alkali Fusion

- Simultaneous assay for Pt and Ru
- Inexpensive Procedure
- Visual hints at quality of assay
- Creates high sodium matrix

Sample Riffled

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Sample weighed into Zirconium crucible along with Sodium Peroxide

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Sample and flux fused over Bunsen Burner until red hot

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Water, Aqua Regia, and tetrafluoroboric acid leach oxidized Pt, Ru

↓

Solution Filtered, Filter paper examined for clarity

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Solution run via ICP-OES

Visual Filter Paper Inspection

Average of all sample sizes: 42.02%

Sample Size (g)	%Ru	
3_1	40.82	Avg
3_2	41.22	41.35
3_3	42.16	RSD
3_4	42.12	2.0%
3_5	39.8	
3_6	41.46	
3_7	41.90	

Alkali Fusion multiple sample sizes

- Best Replicates from the larger sample sizes

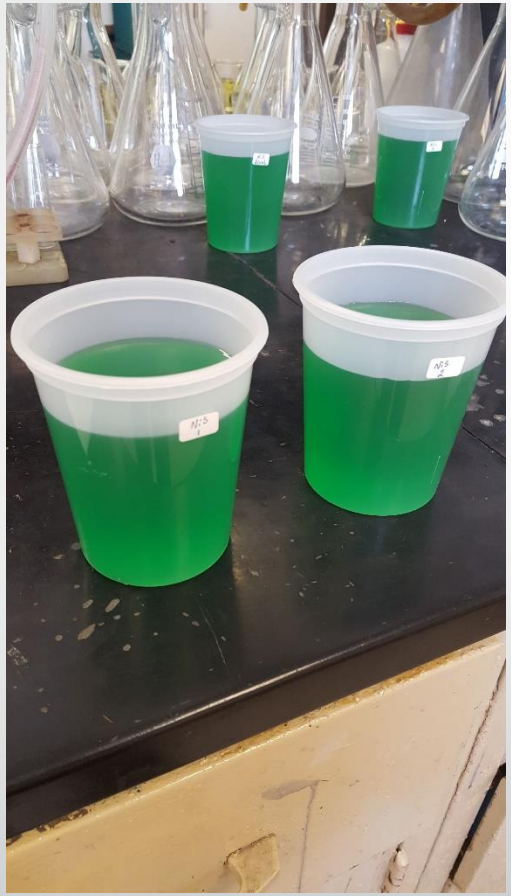
Sample Size (g)	Ru%	RSD
1.00	42.43	0.21%
0.75	41.86	0.33%
0.50	42.45	0.50%
0.25	41.35	2.00%

Alkali Fusion Ru & Pt %

Sample Size (g)	%Ru	RSD	%Pt	RSD
1.00	42.43	0.21%	11.03	0.89%
0.75	41.86	0.33%	11.05	1.49%
0.50	42.45	0.50%	11.32	0.71%
0.25	41.35	2.00%	11.18	1.49%

Nickel Sulfide Fusion

- Fire Assay separation of Ru and Pt simultaneously
- Expensive
- Time consuming



Sample Riffled

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Sample weighed with appropriate flux and fused

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NiS button collected, containing Pt and Ru

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Button Weighed, crushed then dissolved in conc. HCl

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Solution filtered, Pt and Ru precipitated using Sodium Sulfide

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Precipitate filtered, resulting filter paper and residue dissolved in Aqua Regia

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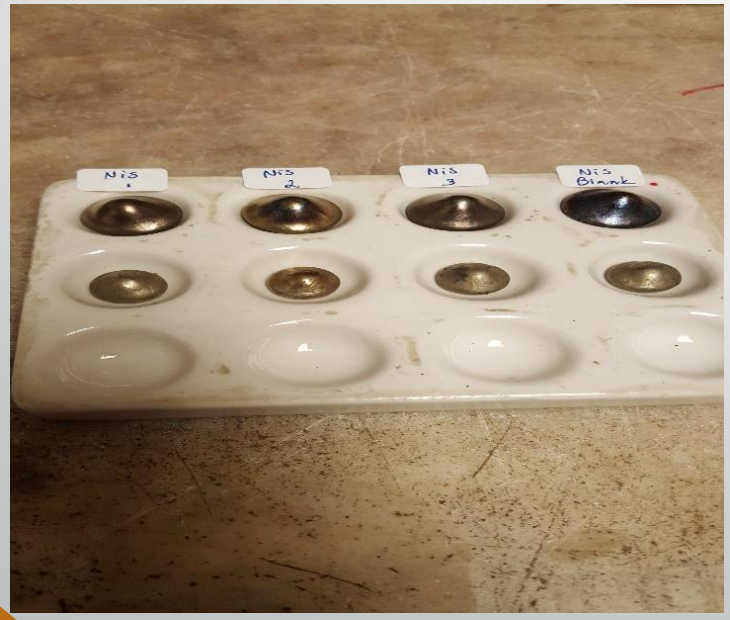
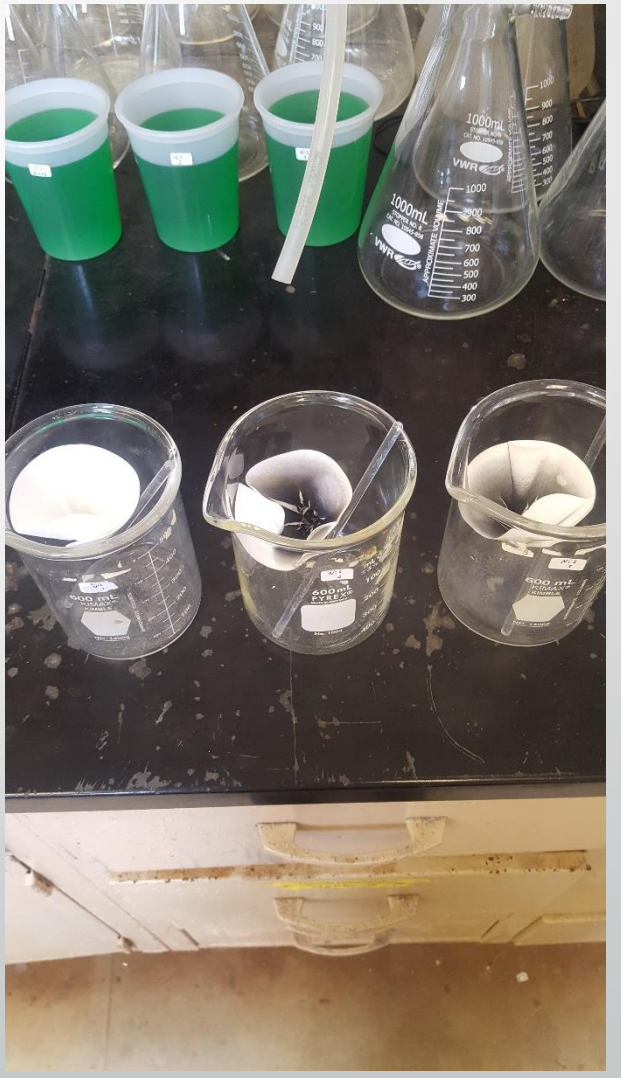
Solution run via ICP-OES

Nickel Sulfide Results

Sample	%Ru	%Pt
1	41.98	11.56
2	19.04	11.42
3	22.65	11.5





Results Across Multiple Assays

Assay	%Pt	%Ru
XRF	9.790%	41.97%
Fire Assay dilution	11.60%	X
Fire Assay concentrated	11.72%	X
Fire Assay Pb matrix	12.12%	X
Alkali fusion ICP-OES	11.16%	42.02%
Alkali fusion AAS	11.08%	41.00%
Direct Dissolve	11.43%	40.29%
NiS Fire Assay	11.49%	41.98%
Average	11.51%	41.45%

Future Directions

- Continue to develop NiS Fire Assay procedure
- Investigate Te Coprecipitation techniques
- Investigate Ru distillation options
- Investigate Pb interference, is it correctable?
- Investigate automated fusion techniques

Questions?