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Optimizing XRF Calibration Protocols for Elemental Quantification of Mineral Solids from Athabasca Oil Sands

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Athabasca Oil Sands

Oil sands mine

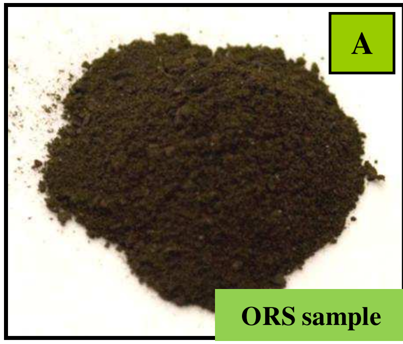
- an open-pit north of Fort McMurray
- produced ~ ¾ of a million barrels a day

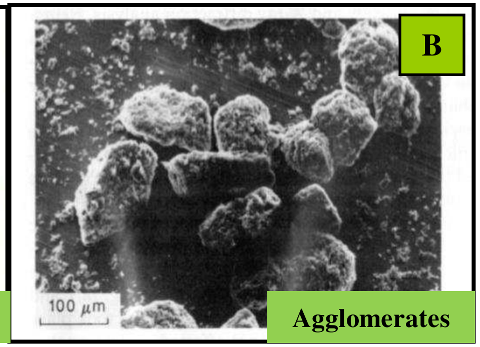
Oil sands being composed of coarse sand, silt and clay solids (80–85%), bitumen (5–15%) and water (1–5%)

Photographs taken from the National Geographic, March 2009

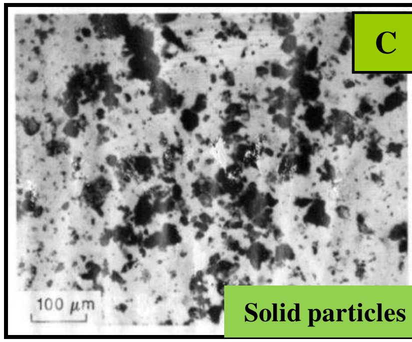
Organic Rich Solid (ORS)

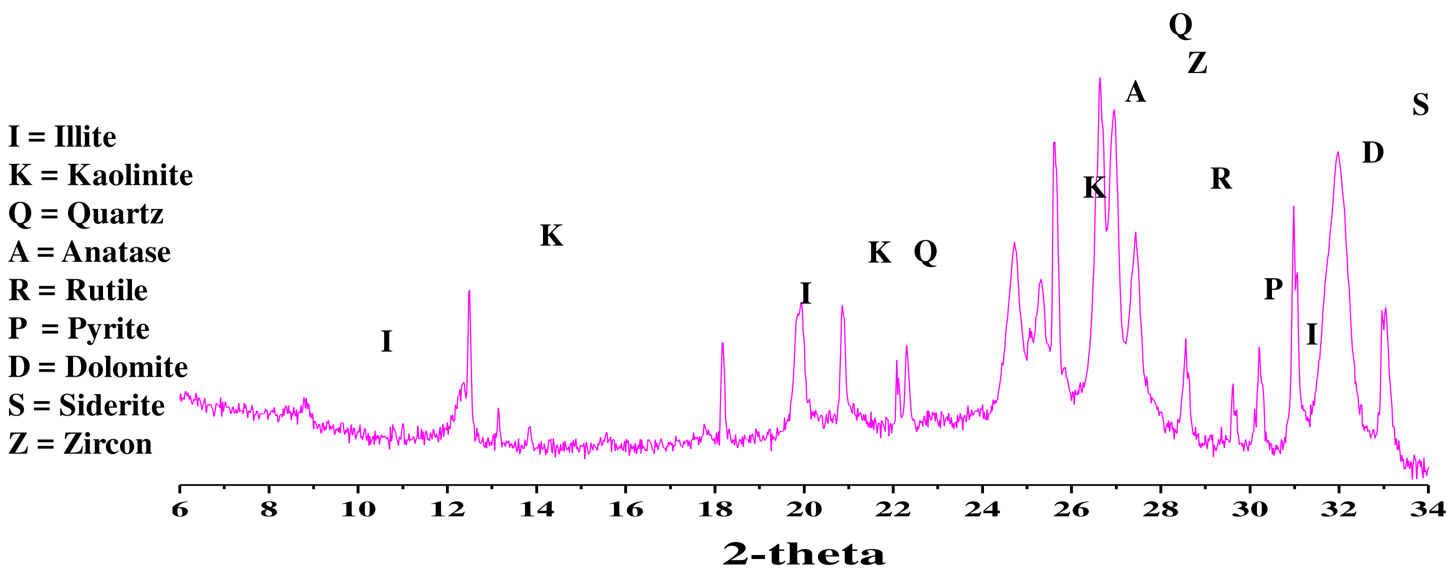
Oil sands + Toluene + Water $\xrightarrow[\text{Centrifuge}]{\text{Agitate}}$ ORS ~ 0.1-0.3g





$\xrightarrow[\text{Plasma Oxidation}]{\text{Low Temperature}}$





Calibration for ORS

Certified Reference Materials

United States Geological Survey (USGS) – 8 standards

BCR-2, BHVO-2, BIR-1, DNC-1,GSP-2, QLO-1, SDC-1, W2-a

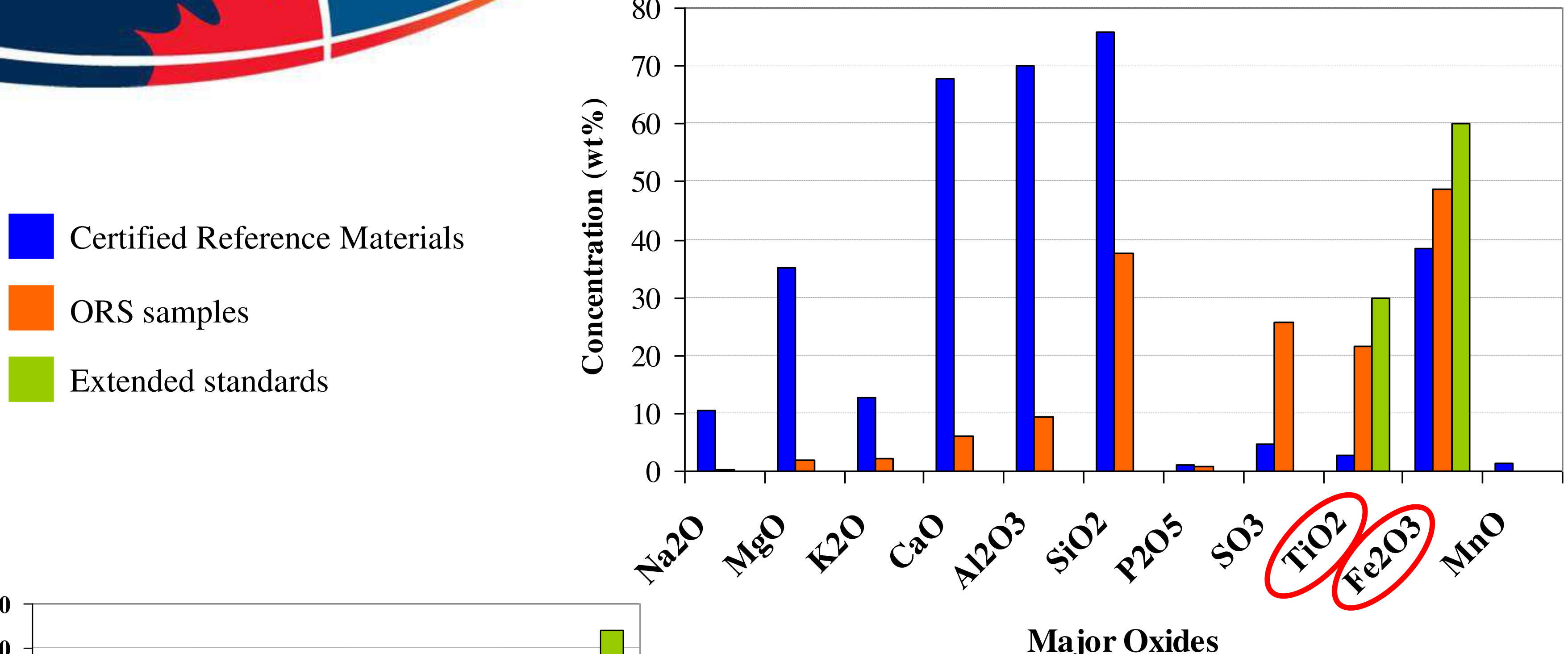
National Institute of Standards and Technology (NIST) – 15 standards

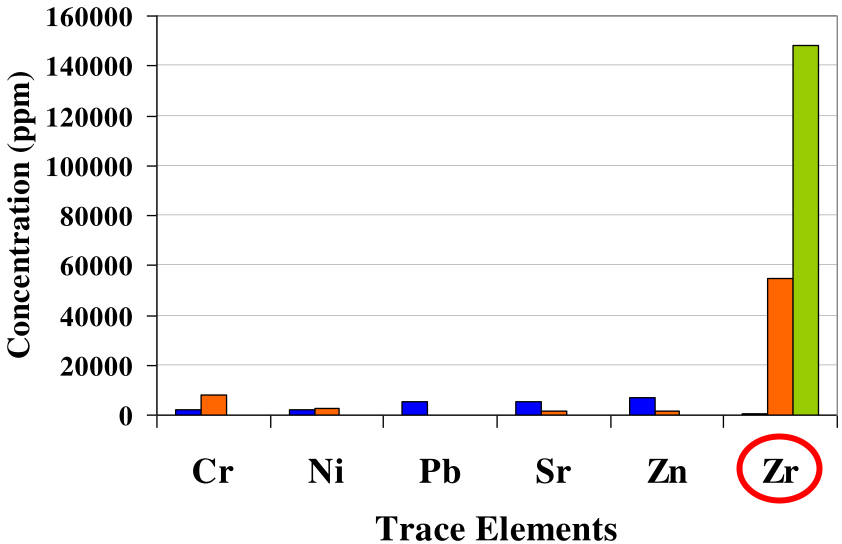
Cement Standards: *SRM1880a, SRM1881a, SRM1882a,*
SRM1883a, SRM1884a, SRM1885a,
SRM1886a,SRM1887a, SRM1888a,
Soil Standards: *SRM2586, SRM2857, SRM2709,*
SRM2710, SRM2711, SRM2782

Centre de la Recherche Scientifique (CNRS) – 16 standards

AC-E, AL-I, AN-G, BE-N, DR-N, DT-N, FK-N, GA, GH,
GL-O, GS-N, Mica-Fe, Mica-Mg, PM-S, UB-N, WS-E

Concentration Range





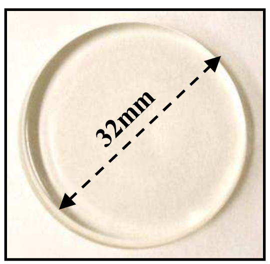
TiO_2 - 99.999%purity, rutile

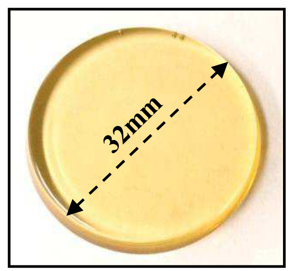
Fe_2O_3 - 99.999%purity, metal basis

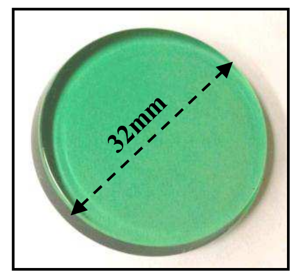
ZrO_2 - 99.99%purity

Sample preparation

3-positions Claisse M4 Fluxer







Claisse 66.67% $Li_2B_4O_7$-32.83% $LiBO_2$-0.5% LiBr

0.1g Sample + 7.0g Flux

Challenges

1. Lack of certified reference materials to cover important elements e.g. Fe, Ti and Zr concentration in ORS
2. Small amount of samples available (100-300mg)
3. High carbon content (LOI ~ 25-30%)

Instrumentation

Bruker AXS S4 Pioneer

4 kW sequential WDXRF with end window and Rh-target X-ray tube

Measurement Conditions

- Vacuum mode
- 28mm mask
- 0.23dg collimator

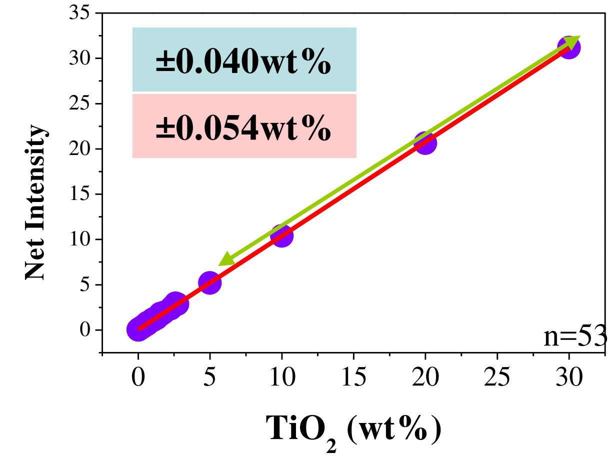
Crystals	Elements
PET	Si, Al
LiF200	Ca, Cr, Fe, K, Ni, Pb Sr, Ti, Zn, Zr
LiF220	Mn
XS-55	Mg, Na
Ge	P, S

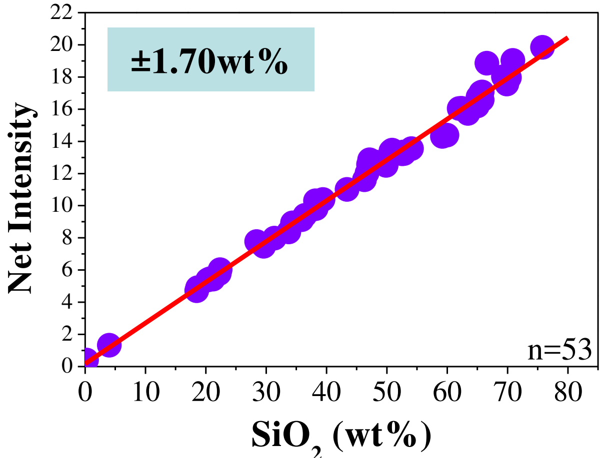
Calibration Curves for ORS

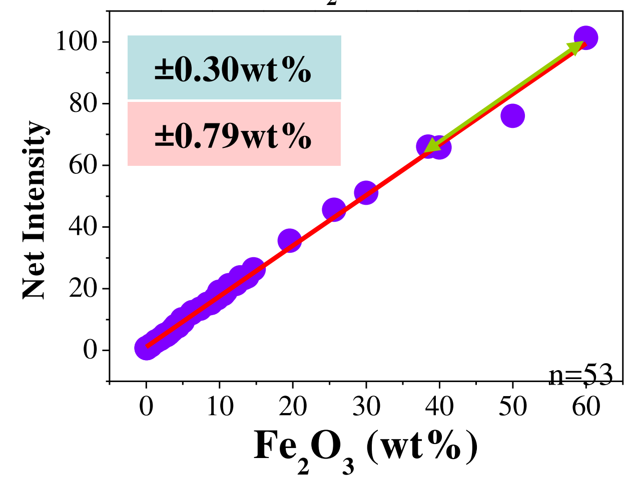
Un-Extended

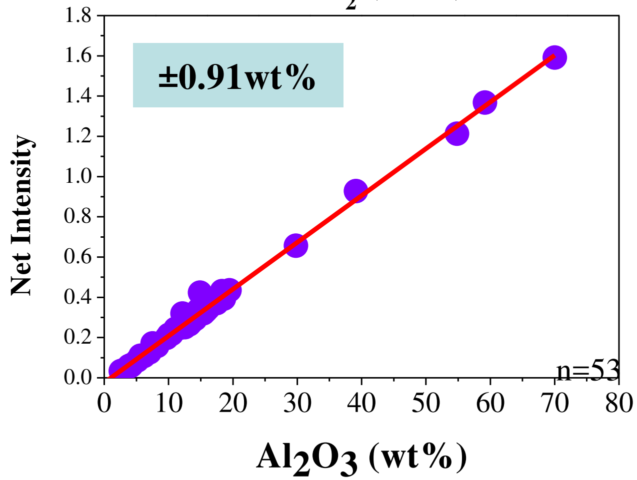
Extended

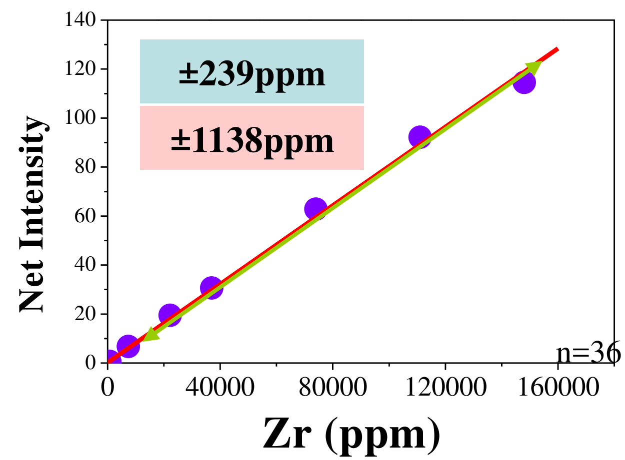
No matrix correction











Accuracy

10 Certified reference materials that were not participated in the calibration

SiO_2 (wt%)			
	Certified Concentration	Calculated Concentration	Absolute Difference
AGV-2	59.30	58.06	**1.24**
BX-N	7.40	6.66	**0.74**
COQ-1	3.47	2.93	**0.54**
DTS-2b	39.40	38.19	**1.21**
NOD-A-1	3.81	3.04	**0.77**
NOD-P-1	13.90	12.98	**0.92**
SCo-1	62.80	61.60	**1.20**
SDO-1	49.28	47.84	**1.44**
SGR-1b	28.24	27.49	**0.75**
ZW-C	54.00	52.86	**1.14**

Al_2O_3 (wt%)			
	Certified Concentration	Calculated Concentration	Absolute Difference
AGV-2	16.91	16.60	**0.31**
BX-N	54.21	54.19	**0.02**
COQ-1	0.37	0.00	**0.37**
DTS-2b	0.45	0.03	**0.42**
NOD-A-1	3.87	3.83	**0.04**
NOD-P-1	4.80	4.83	**0.03**
SCo-1	13.70	13.44	**0.26**
SDO-1	12.27	11.81	**0.46**
SGR-1b	6.52	6.03	**0.49**
ZW-C	18.45	18.35	**0.10**

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Accuracy

Fe_2O_3 (wt%)			
	Certified Concentration	Calculated Concentration	Absolute Difference
AGV-2	6.69	6.67	**0.02**
BX-N	23.17	24.33	**1.16**
COQ-1	2.94	2.77	**0.17**
DTS-2b	7.76	7.97	**0.21**
NOD-A-1	15.60	15.05	**0.55**
NOD-P-1	8.30	8.20	**0.10**
SCo-1	5.13	5.03	**0.10**
SDO-1	9.34	9.46	**0.12**
SGR-1b	3.03	2.79	**0.24**
ZW-C	9.46	9.50	**0.04**

10 Certified reference materials that were not participated in the calibration

TiO2 (wt%)			
	Certified Concentration	Calculated Concentration	Absolute Difference
AGV-2	1.05	1.02	**0.03**
BX-N	2.37	2.37	**0.00**
COQ-1	0.15	0.13	**0.02**
DTS-2b	0.00	0.00	**0.00**
NOD-A-1	0.53	0.45	**0.08**
NOD-P-1	0.50	0.43	**0.07**
SCo-1	0.63	0.57	**0.06**
SDO-1	0.71	0.68	**0.03**
SGR-1b	0.25	0.23	**0.02**
ZW-C	0.05	0.03	**0.02**

Bitumen-Free Solids (BFS)

- Processability of oil sands
- Recovery of heavy metals
- Recycle of oil sands tailing

Oil sands

Soxhlet – Dean and Stark extraction with toluene

Water 1-5%

Bitumen-Free solids 80-85%

Extracted Bitumen 5-15%

Disperse in 0.1%w/w of $Na_4P_2O_7$

Screen through standard sieve

Fraction 1 >212um

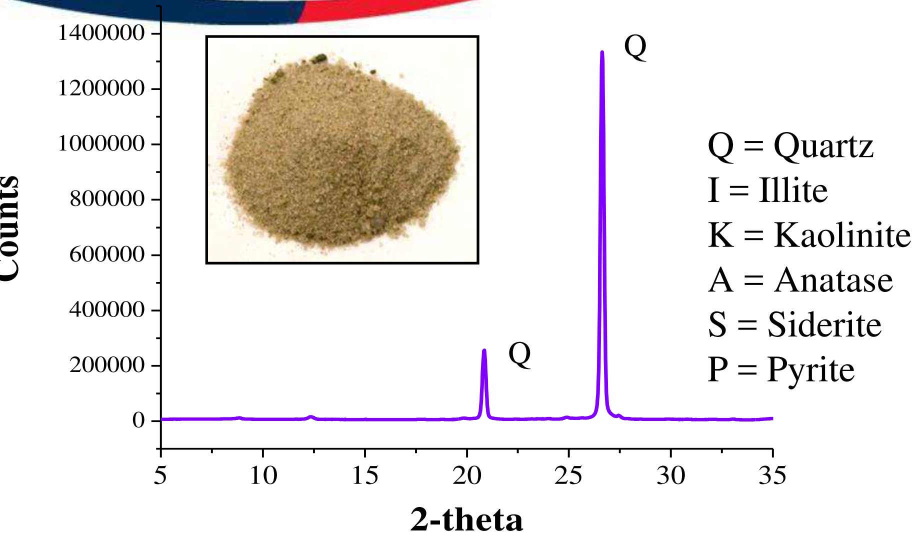
Fraction 2 150-212um

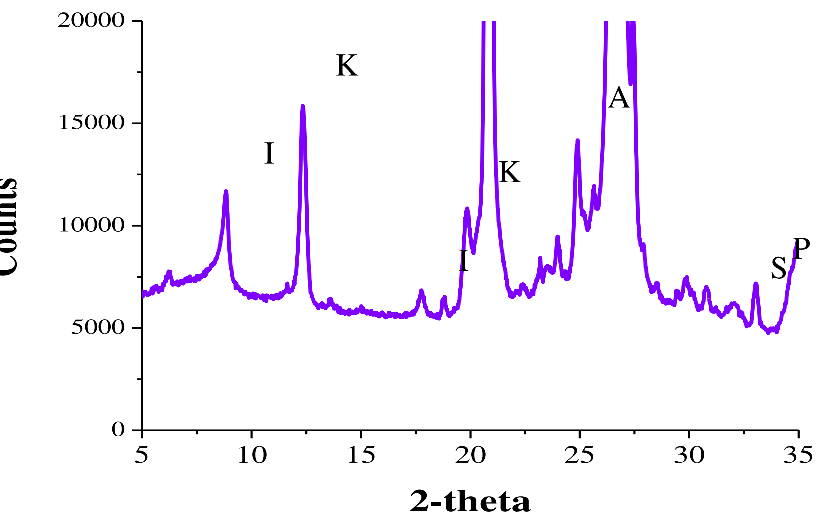
Fraction 3 75-150um

Fraction 4 45-75um

Fraction 5 <44um

Calibration for BFS





Calibration Range

Major Oxides	Min (wt%)	Max (wt%)
SiO_2	90	100
Al_2O_3	0	5
Minor Elements	**Min (ppm)**	**Max (ppm)**
Mg	0	10000
Ca	0	10000
Ti	0	10000
Cr	0	10000
Mn	0	10000
Fe	0	10000
Ni	0	10000
Zr	0	10000
Zn	0	10000
K	0	10000

Sample preparation

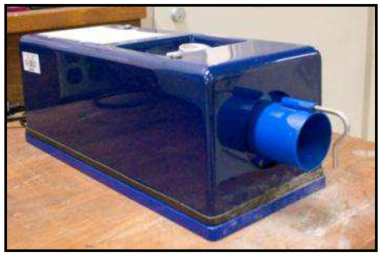
23 Standards → Weigh and mix different oxides concentrations

10g of oxide mixtures + 25 mL of isopropanol

Wet grinding – 5 min

Air dry for 24 hrs

Fusion
1.0g Sample + 7.0g Flux



McCrone Micronizing Mill

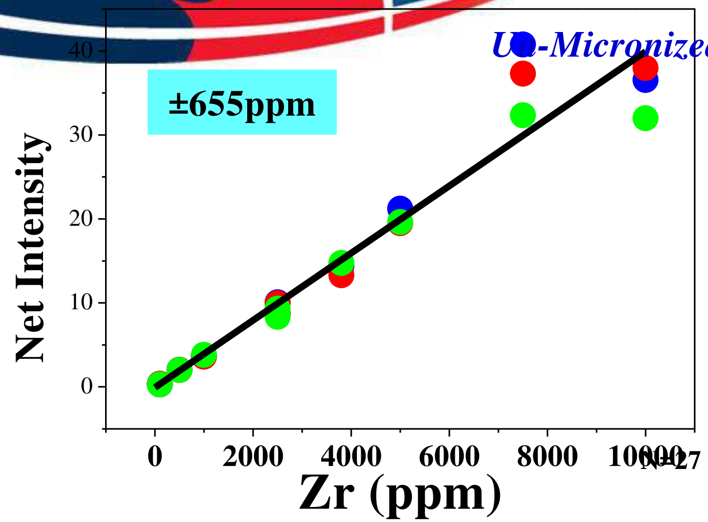
Oxides	Purity
SiO_2	99.995% metals basis
Al_2O_3	99.998% metals basis
MgO	99.999%
CaO	99.995%
TiO_2	99.999%, rutile
Cr_2O_3	99.9%
MnO	99.99+% metals basis
Fe_2O_3	99.999% metals basis
NiO	99.999% metals basis
ZrO_2	99.99%
ZnO	99.999% metals basis
K_2CO_3	99.995%

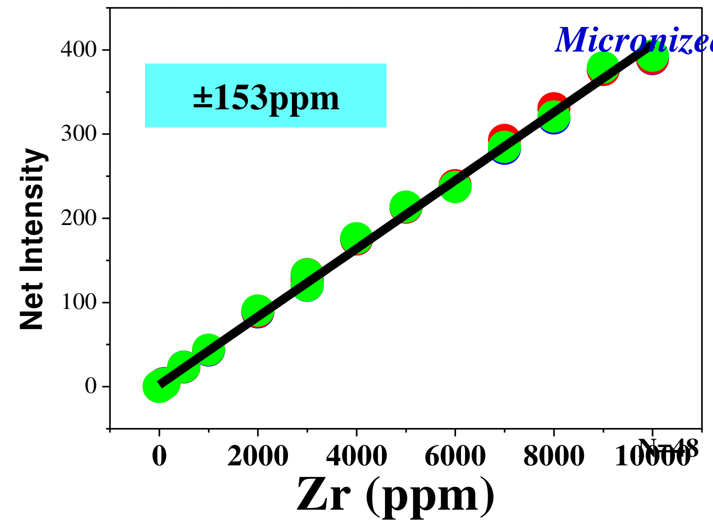
Claisse 66.67%$Li_2B_4O_7$-32.83%$LiBO_2$-0.5%LiBr → Un-dissolved particles

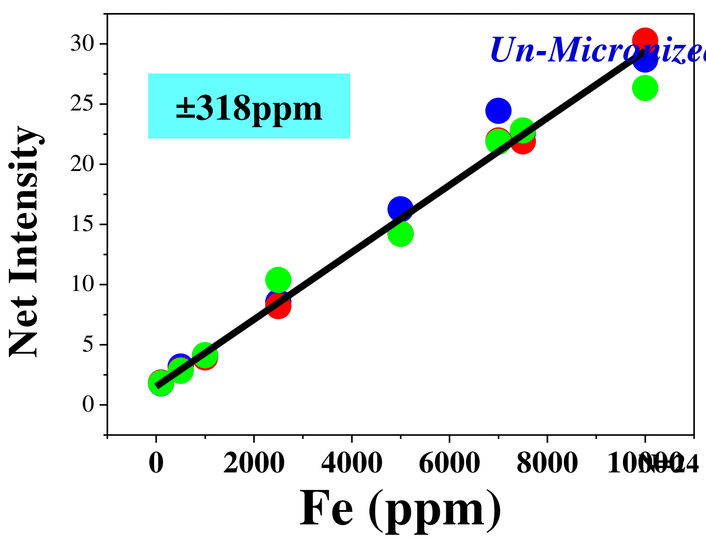
Claisse 49.25%$Li_2B_4O_7$-49.25%$LiBO_2$-0.5%LiBr → Perfect beads

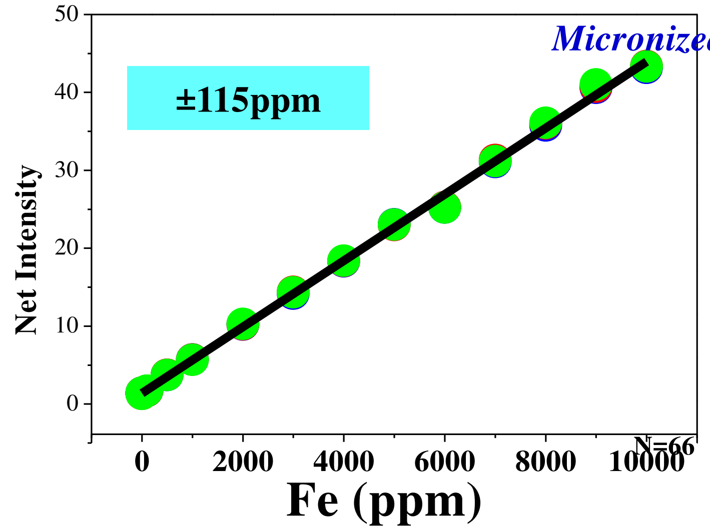
Claisse 34.83%$Li_2B_4O_7$-64.67%$LiBO_2$-0.5%LiBr → Crystallization

Why Micronizing?









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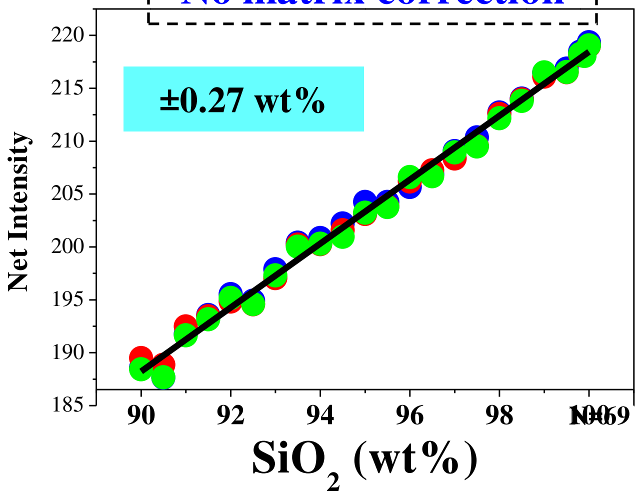
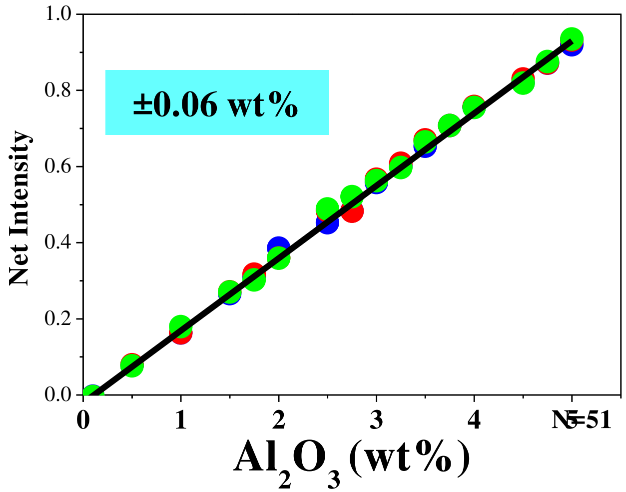
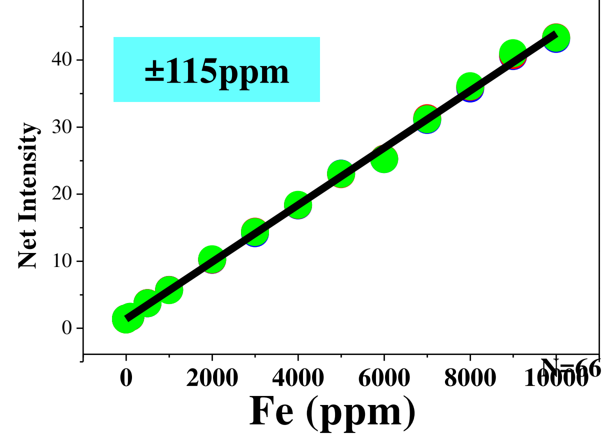
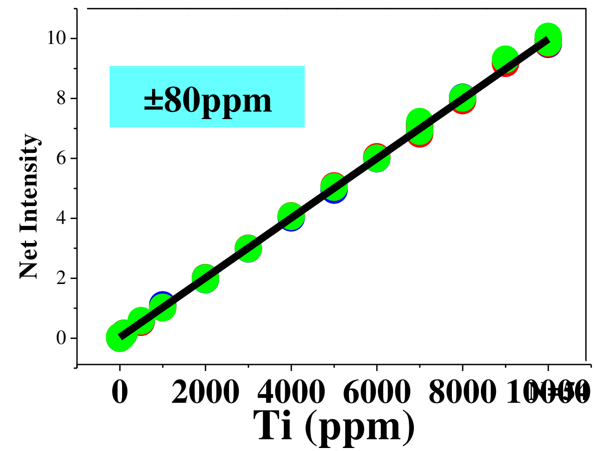
Calibration Curves for BFS

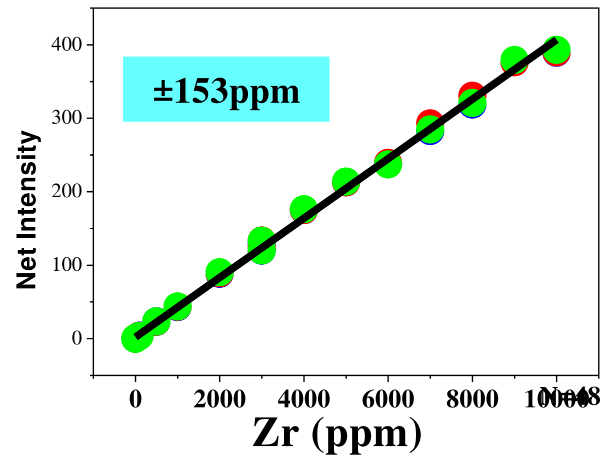
No matrix correction



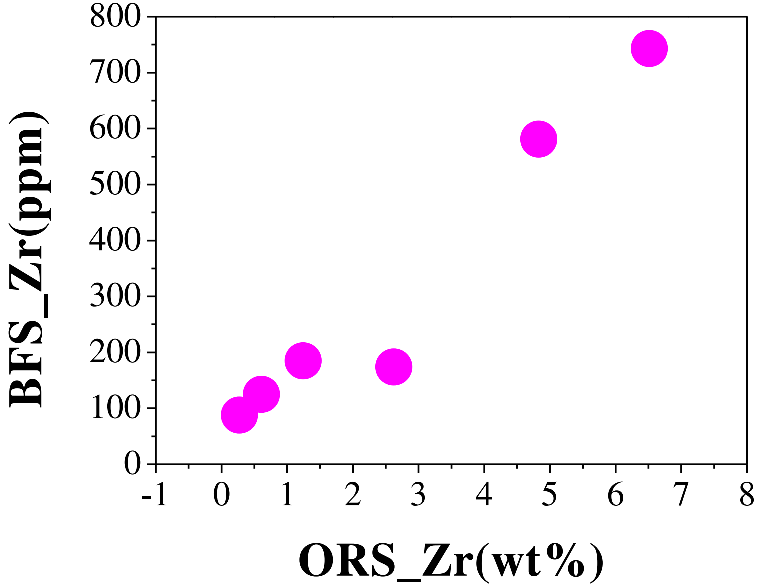


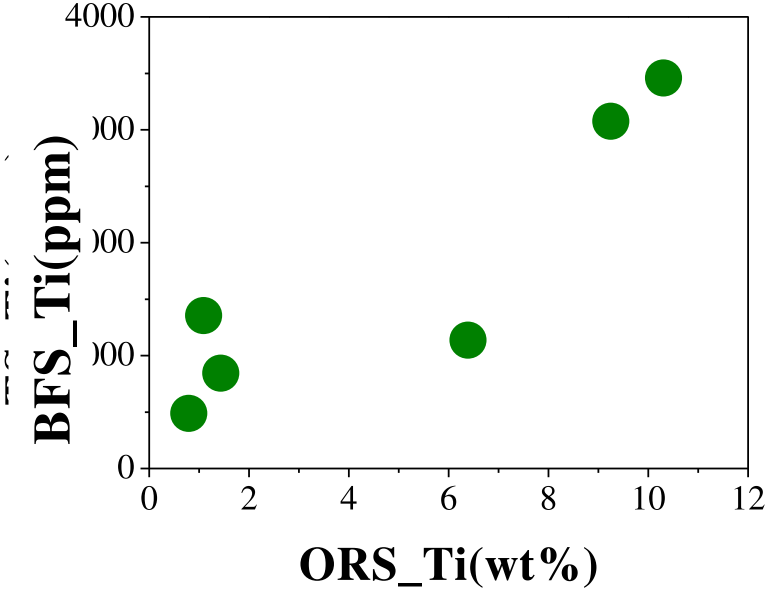






Results Correlation





- Zr and Ti content in BFS and ORS samples compared
- More data is required to determine the relationship

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Conclusion

- Optimized the calibrations for two types of mineral solids in oil sands
- Able to achieve good precision and accuracy in the calibrations without matrix correction
- Discover some correlation that could be a possible marker for oil sands recovery
- Potential applications in mineral recycling and heavy metal recovery from oil sands tailings
- Future work: quantification of heavy metal in oil sands bitumen (Ni, V, Fe)

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