Improvements in iridium target chemistry

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Outline

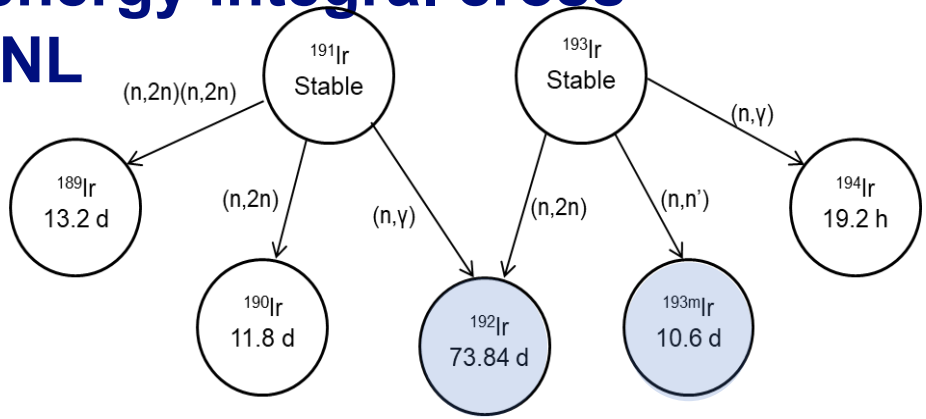
- Research goals
- Background
  - Iridium as a radiochemical detector
- Iridium Chemistry
  - Previous chemistry
  - New method and application to irradiated Ir pellets
  - Results and conclusions
- Fusion of Iridium Foils
  - Background
  - Method development using cold foils and application to hot foils
  - Results and conclusions
- Future work

Research Goals-

1. Make improvements to previous Ir chemistry method used at LANL and apply to Ir pellets

2. To develop a method for the dissolution and purification of irradiated Ir foils for measurement with a silicon drift detector

Iridium is an important radiochemical detector used to provide a spectral index for energy integral cross section measurements at LANL



- **Monitor 3 spectral groups at once**
  - Thermal/epithermal
  - 14 MeV
  - Neutrons in the fission spectrum >2 MeV
- **Understand the neutron fluence a sample has been exposed to over the course of irradiation** [1]
- **Spectral Index ^{193}Ir(n,n')^{193m}Ir/^{191}Ir(n,γ)^{192}Ir –hardness of neutron spectrum**
  - Ratio of fast neutrons (En>1MeV) to thermal neutrons (En<1MeV)

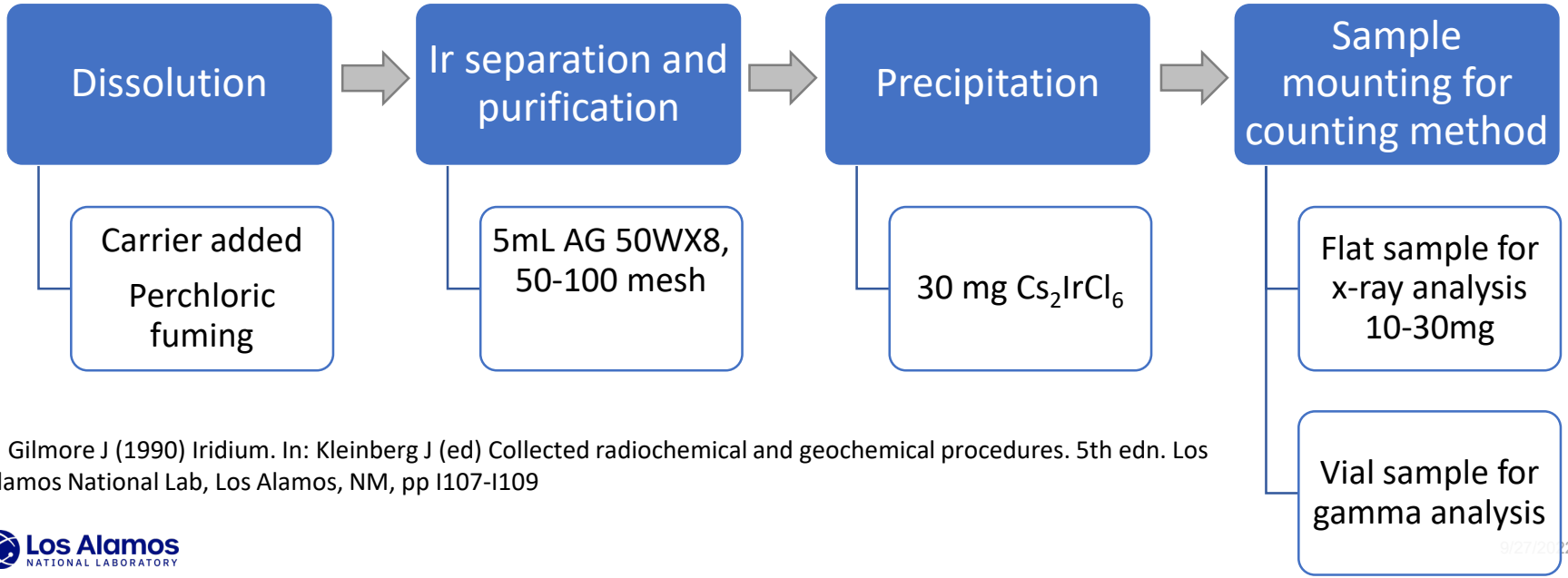
1. Lee AS (2016) Determination of the Spectral Index in the Fission Spectrum Energy Regime. Los Alamos National Lab.(LANL), Los Alamos, NM

Research Goal- 1. Make improvements to previous Ir chemistry method used at LANL

- **Safer**
  - Eliminates use of perchloric and hydrofluoric acid
- **More efficient**
  - Iridium short half-lives
    - Days
- **Qualitative study**- compares the results of previous chemical method and new method when applied to irradiated Ir pellets.
  - Previous results from old lab notebooks
- **Importance:** This research will improve the overall quality of the Ir data while providing a faster safer method for the analysis of Ir isotopes.

Previous Iridium chemistry at LANL

- Derived from Gilmore – underground nuclear test debris samples [2]
- Modified Moses Attrep Jr



2. Gilmore J (1990) Iridium. In: Kleinberg J (ed) Collected radiochemical and geochemical procedures. 5th edn. Los Alamos National Lab, Los Alamos, NM, pp I107-I109

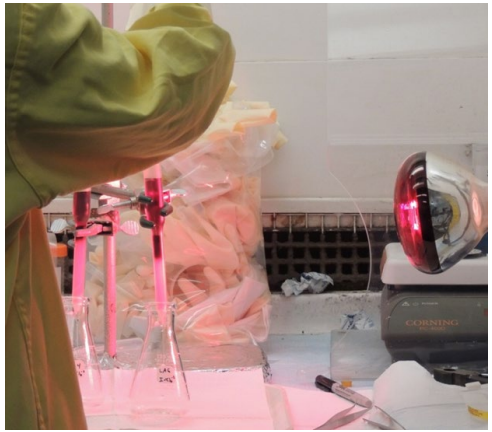
Changes focused on replacing the dissolution and the first column of the procedure

Perchloric Fuming

- Purpose- dissolve sample and adjust oxidation state of Ir to +4 for cation column prep [2,3]
- Issues-
  - Hazardous chemical
  - Lengthy and tedious
  - Specialized hood
    - Scheduled for use
    - Cleaned
- **Replace with HCl dissolution to prepare for anion column [4]**

1st Cation Exchange column

- Purpose- remove contaminants
- Issues-
  - Tedious
  - Uses hazardous chemicals



3. Fine DA (1970) Studies of the iridium(III) and (IV)—chloride system in acid solution. Journal of Inorganic and Nuclear Chemistry 32 (8):2731-2742. doi:https://doi.org/10.1016/0022-1902(70)80323-2
4. Evers AP, Edwards RI, Fieberg MM (1978) Recovery and purification of iridium. United States Patent

Experimental- Column Chemistry

Column1: AG MP-1M, 50-100 mesh – 10 and 20mL column

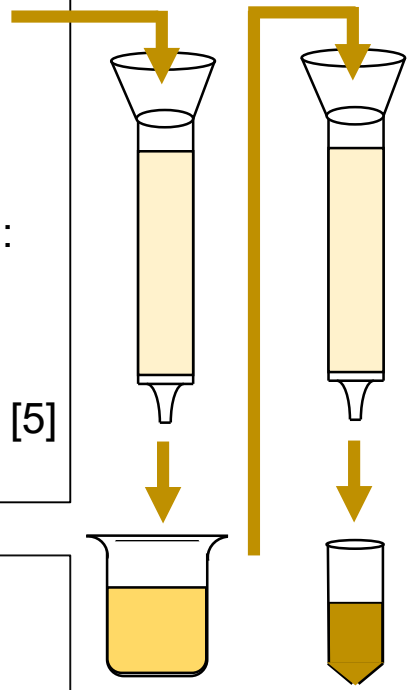
1.) Load: 10mL Ir 3M HCl: $IrCl_6^{2-}$

2.) Wash: 5x column vol. 6M HCl: removes K and impurities

3.) Elute Ir: 50mL 9M HBr: $IrBr_6^{2-}$ [5]

4.) Evaporate eluant

5.) Dry down 3x with 10mL 12M HCl ; $IrCl_6^{2-}$



Column 2: AG 50WX8, 50-100 mesh – 5mL column [2]-

6.) Reconstitute sample in 0.05M HCl and Load onto column

- Ir does not interact with column

7.) Wash: 10mL 0.05M HCl

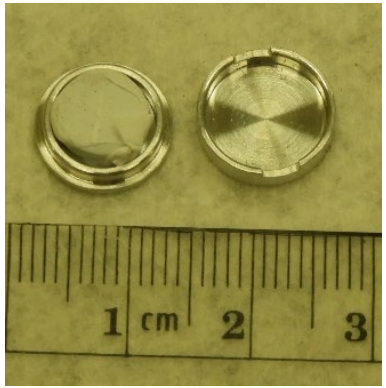
- removes any cations in sample

5. Bond EM, Moody WA, Arnold C, Bredeweg TA, Jandel M, Rusev GY (2016) Preparation of iridium targets by electrodeposition for neutron capture cross section measurements. Journal of Radioanalytical and Nuclear Chemistry 307 (3):1981-1986. doi:10.1007/s10967-015-4607-2

Experimental- 10 Ir pellets analyzed

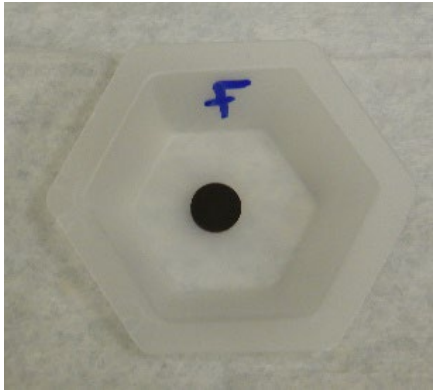
Pellets prepared with KBr press

- KBr press 7mm die
- ~90mg
- 60% KCl and 40% K_2IrCl6
- 37.3% ^{191}Ir and 62.7% ^{193}Ir



After Irradiation

- pellets are **weighed**
- **chemically digested** in 10 mL 3M HCl for 1-1.5 hours.



Ir Separated and purified with two columns.

- Column 1 – 10 and 20mL
- Sample separated to two equal volumes
- Brought to 6M HCl

Experimental- 10 pellets analyzed

Precipitated as Cs_2IrCl_6

- 1mL of CsCl solution added to each sample
- A few drops of conc. HNO_3 to keep Ir in +4 state
- Left on hotplate at 90° C overnight.

Precipitate cleaned

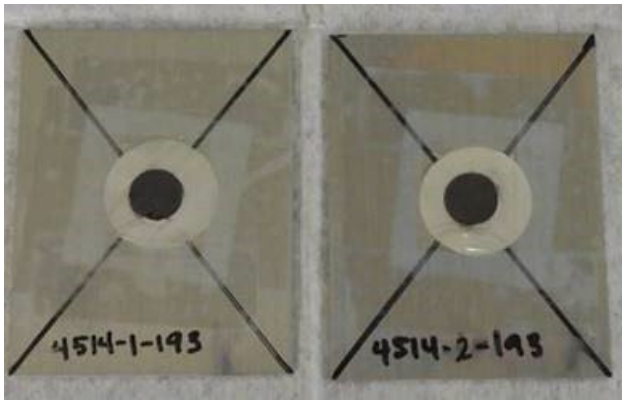
- Centrifuged for 10 min.
- 10mL of 6M HCl added
  - Centrifuged
- 10mL of EtOH added
  - Centrifuged and this step is repeated

One sample **Filtered**

- Whatman Grade 50 filter paper
- Dried and weighed
- 3 drops of rubber cement solution added
- Dried

Mounted [6]

- With double sided tape to 3x5” Al plate
- Covered with Mylar film



6. Attrep MJ, Bowen SM, Smith JE (2001) Preparing Samples for Beta Counting Los Alamos, NM

Results and Conclusions- New method can replace previous method

- **New method produces samples of similar mass**
  - New method- **13-25 mg,** average of **18 ± 4 mg**
  - Previous method- **12-25 mg,** average of **20 ± 5 mg**
  - %Precipitate recovery for half the sample for new method is **36 ± 7%** and previous method is **27 ± 6%**
- **Decreased method time- reduces method by two days for processing 2 samples**
  - New method- dissolution takes 1-1.5 hours vs full working day
  - 10mL column takes 1 hour
  - 20mL column takes 2 hours (equivalent to previous method)
- **Increase Safety- eliminated the use of perchloric acid in the method**

Research Goal- To develop a method for the dissolution and purification of irradiated Ir foils for measurement using an SDD

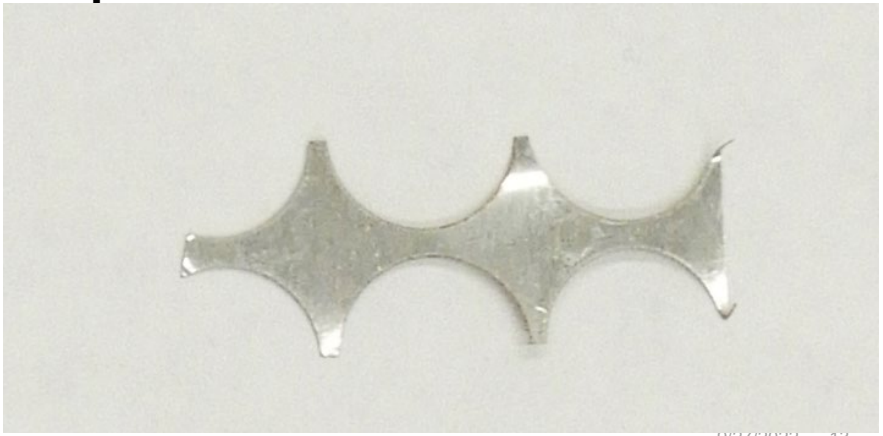
- **Motivation**
  - High E irradiations produced insoluble residue
  - Teflon fused to pellet, making dissolution/chemistry more difficult
- **Method development**
  - Cold Ir foil
  - Applied to hot foils and run through separations procedure to determine yields
- **Importance:** Ir foils replace Ir pellets in high irradiation experiments

Ir foil is difficult to digest

Ir not attacked by any acid or aqua regia at cold, normal and boiling temperatures [7]

Develop a method that will consistently completely digest Ir foil using a Meker burner

- **Literature – salt fusions of Ir foil and Ir metal powder**
  - incomplete digestions [5,8]
  - no mention of digestion completeness [7,9-11]

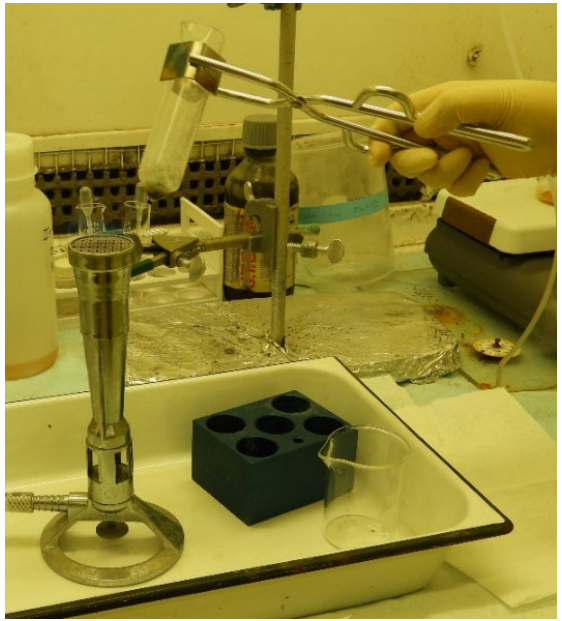


Piece of Ir foil

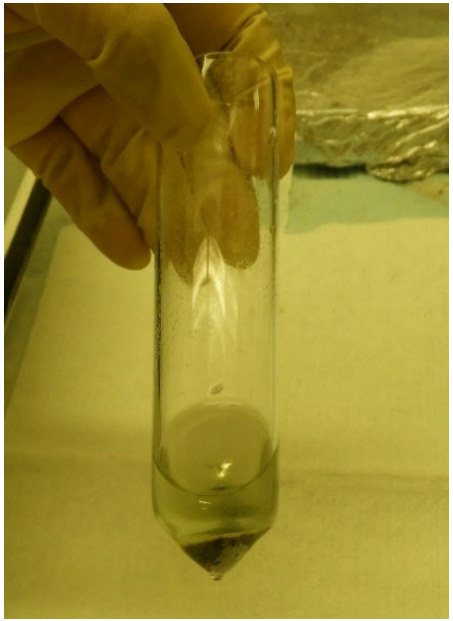
7. Leddicotte GW (1961) The radiochemistry of iridium. United States. Doi: https://doi.org/10.2172/4834231
8. Tinker ND, Zweit J, Sharma HL, Downey S, McAuliffe CA (1991) Production of No-Carrier Added 191Pt, a Radiolabel for the Synthesis and Biological Investigations of Platinum Anti-Tumour Compounds. Radiochim Acta 54 (1):29-34. doi: https://doi.org/10.1524/ract.1991.54.1.29
9. Silver GL (1975) The dissolution and recovery of iridium in a nitrate system. Journal of the Less Common Metals 40 (2):265-267. doi:https://doi.org/10.1016/0022-5088(75)90069-7
10. Johns MW, Nablo SV (1954) Disintegration of Ir 192 and Ir 194. Physical Review 96:1599-1607
11. Despotopulos JD, Kmak KN, Shaughnessy DA (2018) Production and isolation of 197m,gHg. Journal of Radioanalytical and Nuclear Chemistry 317 (2):985-989. doi: https://doi.org/10.1007/s10967-018-5927-9

Method Development- Cold Foils

- 0.025 mm thick Ir foils from Goodfellow
- KOH/KNO_3 1:1, heating strongly over burner for 10 minutes [5,8]
  - Vessel: quartz tube, porcelain crucible
  - Weight: 2-7 mg foils
  - Time: 10-60 min
  - Agitation
  - Capped on a triangle
- Yields determined by weight



Ir foil fusion

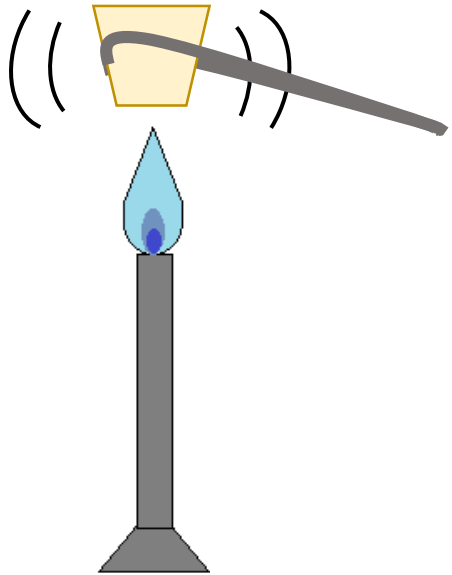


Fused foil

Method development- Cold foils- Results

- Increase time under fusion → increase yield fused
  - Only if agitated
- Agitation is important
  - Prevents Ir embedding in vessel
- Quartz tube malleable >20 min

- **100% fusion- 5mg foils**
  - Constant agitation
  - Uncapped porcelain crucible
  - 20-30 minutes
  - KOH/KNO_3 1:1 ~2g each



Method Overview- Application to hot foils

Fusion – 5.2, 5.2 and 5.7mg foils

- Porcelain crucible, KOH/KNO_3 1:1 2g, 30 min, constant agitation
- Leach crucible with HCl and DI
- Transfer to beaker
- Covert to chloride form 3x 10-20mL conc. HCl

Filter

- Reconstitute 3M HCl
- Filter 541 Whatman filter

Ir separate and purify from leachate [2,5] with two columns
Reconstitute 3M HCl

- Column1: Anion- AG MP-1M
- Column 2: Cation- AG 50WX8

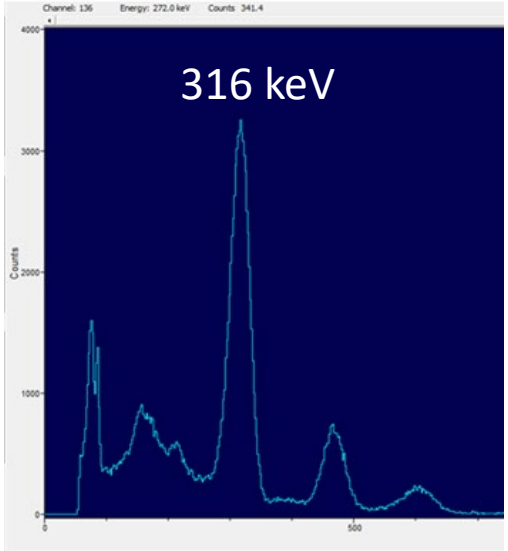
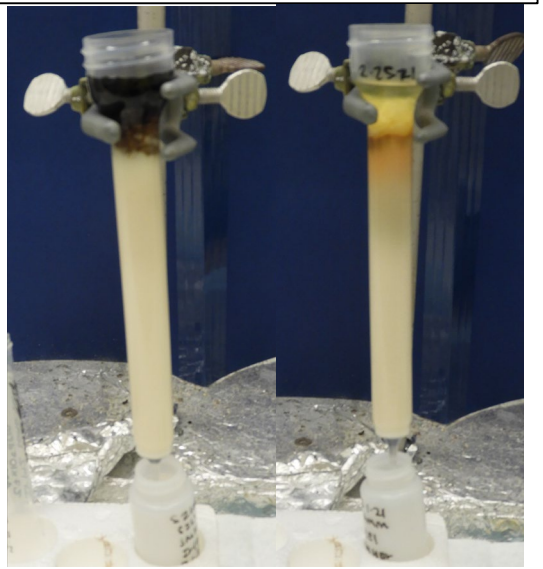


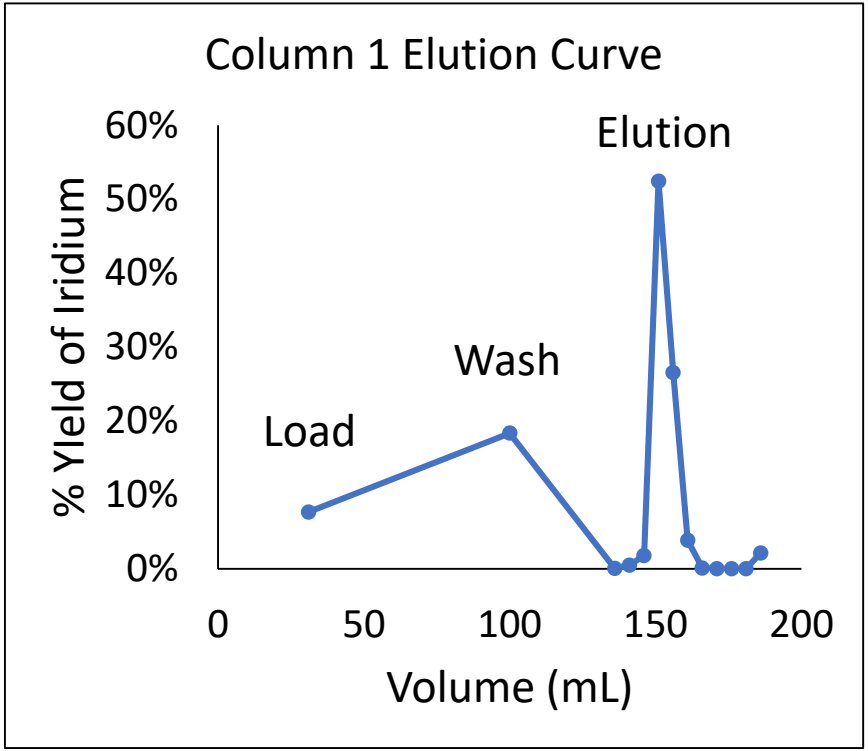
Image is of a Peak Easy spectrum of ^{192}Ir full energy peak 316 MeV with an intensity of 83%.



Column 1: Left: loading Ir in 3M HCl. Right: Eluting Ir with 9M HBr

Results and Conclusions

- **Successfully applied fusion method to foil ~5mg range**
  - Average in leachate- 86±1%
  - Lost to filter- 2%±1%
- **Column 1(Anion)-** 82% 30mL of elution
- **Losses**
  - load and wash
    - Could be associated with Ir+3 not fully oxidizing to the extractable complex of $IrCl_6^{2-}$ instead, forming mixed aquo-chloro complexes [4].
  - Crucible
- **Column 2 (Cation)-** 100% yield



Future Work

- **Understand losses and optimize column 1 for pellet and foil purifications**
  - Oxidation adjustment experiments

- **Include foil in an irradiation with pellet**
  - Process for analysis by Silicon Drift Detector
  - Compare results of foil and pellet

Acknowledgements

- Marian Jandel- UMass Lowell for irradiating foils

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References

1. Lee AS (2016) Determination of the Spectral Index in the Fission Spectrum Energy Regime. Los Alamos National Lab.(LANL), Los Alamos, NM

2. Gilmore J (1990) Iridium. In: Kleinberg J (ed) Collected radiochemical and geochemical procedures. 5th edn. Los Alamos National Lab, Los Alamos, NM, pp I107-I109

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Questions????

1st Cation Exchange Column

1.) **Load** in 1 M $HClO_4$

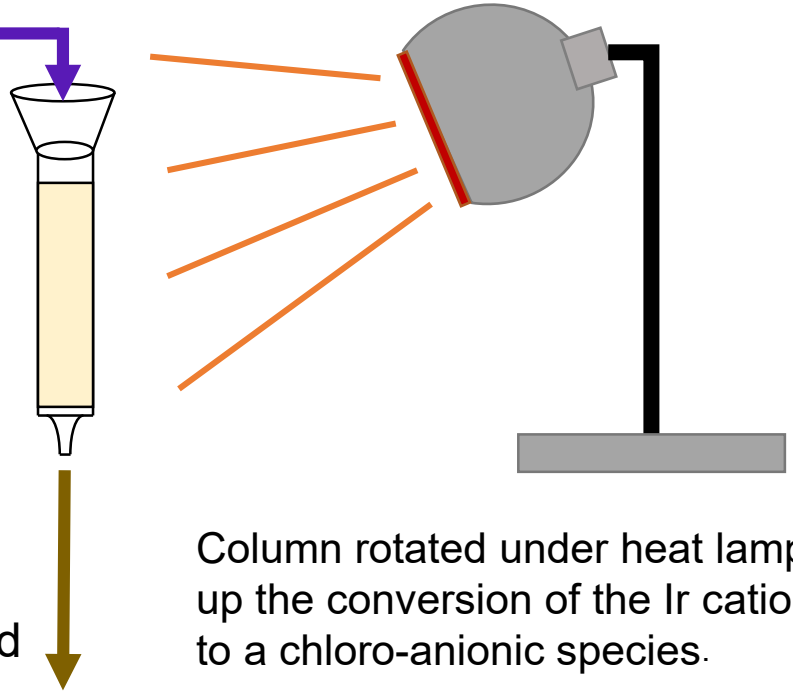
*$Ir(H2O)_6^{4+}$ adheres to column

2.) **Wash** with 1 M HCl + 0.1M HF and 1 M HCl

*Removes ClO_4^- anions

3.) **Elute** Ir with hot 4.5M HCl

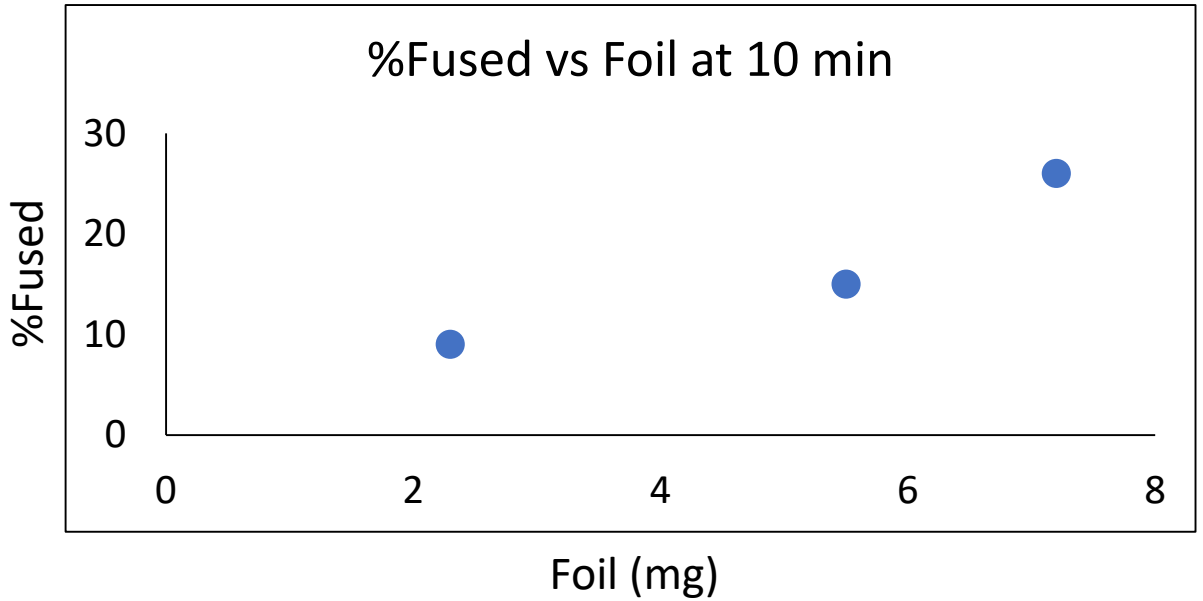
*converts cationic species to mixed anionic Ir^{4+} species



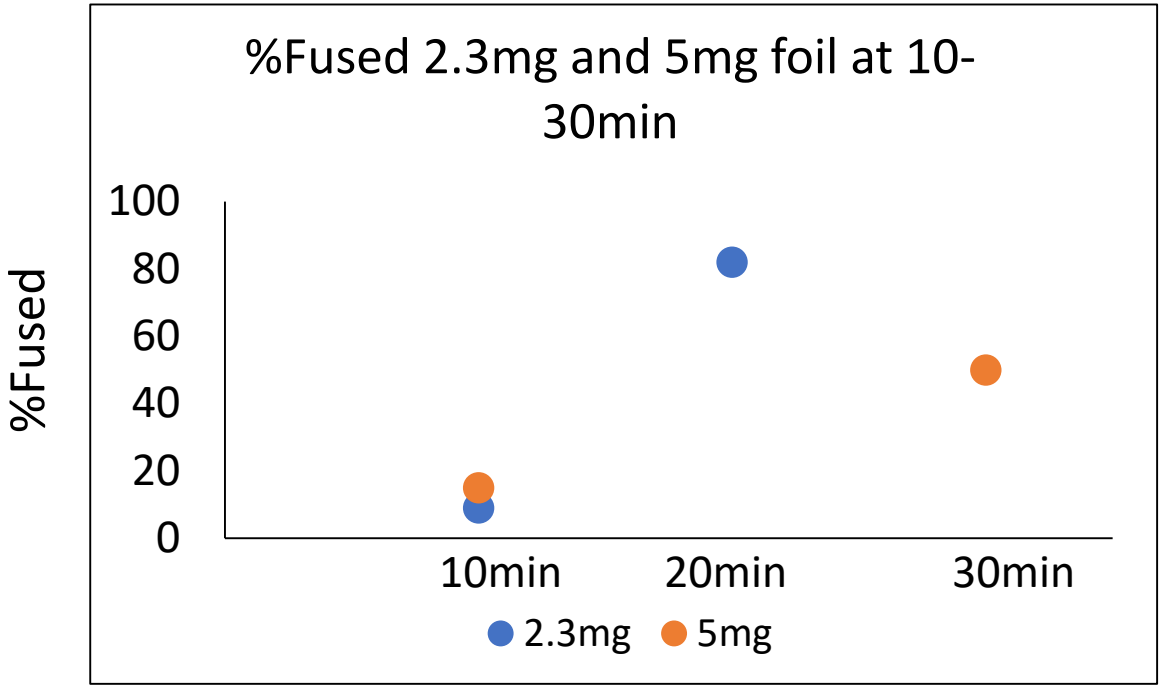
Column rotated under heat lamp to speed up the conversion of the Ir cationic species to a chloro-anionic species.

Method development – varying masses, same time under fusion

KOH/KNO3 1:1, heating strongly over burner for 10 minutes with constant agitation in a quartz tube



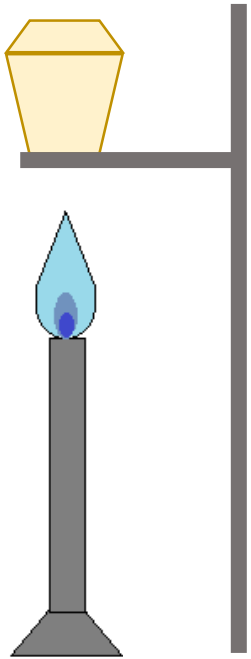
Method development- increase time under fusion



Time dependent- Increase time under fusion → increase fusion yield

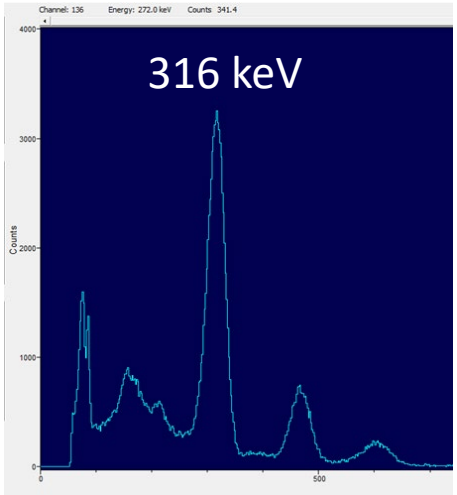
Method development- Mimic fusion in an oven

- Quartz tube malleable >20min
- Switched to a capped ceramic crucible, set on triangle over burner
  - 4mg, 30 min, 8% fused
  - 3.7mg, 60 min, 14% fused
- With no agitation, the foil becomes embedded in crucible



Method can be applied to Ir salt pellets

- Column 1- 75% yield
  - The loss could be associated with Ir+3 not fully oxidizing to the extractable complex of $IrCl_6^{2-}$ instead, forming mixed aquo-chloro complexes [4].
- Column 2- 100% yield



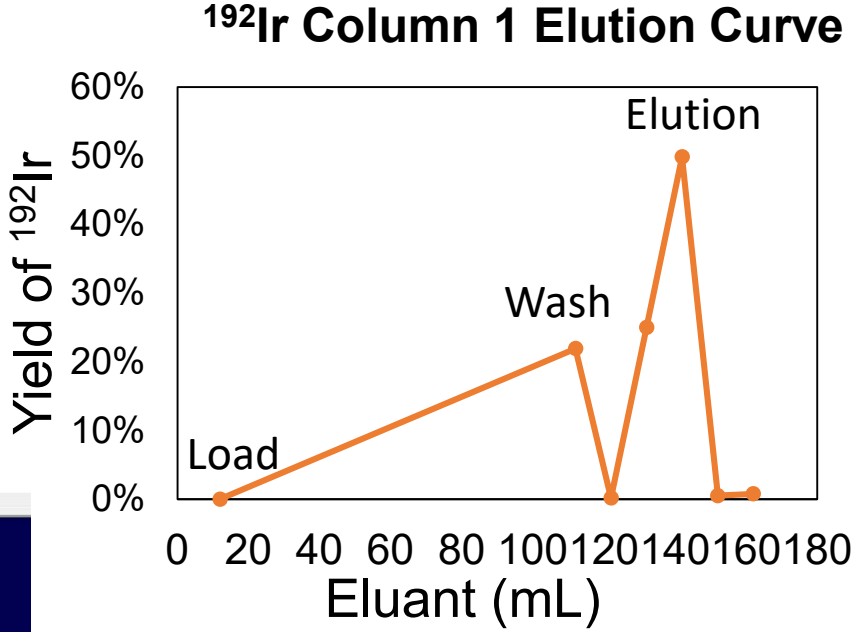
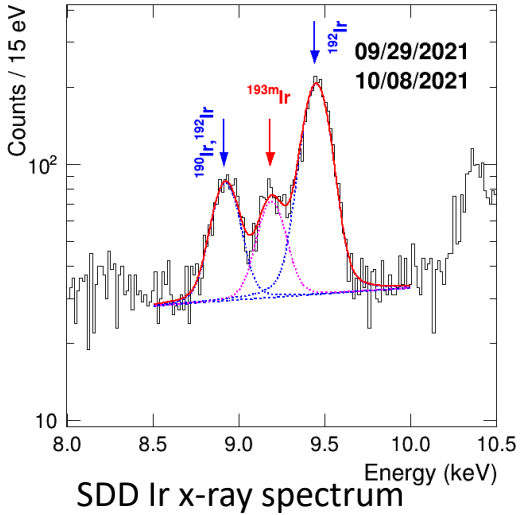


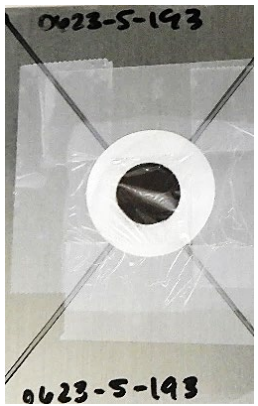
Image is of a Peak Easy spectrum of ^{192}Ir full energy peak 316 MeV with an intensity of 83%.

Radiochemically pure Ir sample for measurement

- Iridium is measured using a Silicon Drift Detector
  - Measure Low E x-rays ^{193m}Ir 9.2keV and ^{192}Ir 9.4keV
- Purification of Ir from Ir pellets
  - Cesium hexachloroiridate (Cs_2IrCl_6) precipitate
  - Self-attenuation
  - Remove elements with same x-ray energies (Os and Pt)
  - Remove K which interferes with precipitate formation



SDD Ir x-ray spectrum



Cs_2IrCl_6 precipitate on filter for counting 11mm diameter


SDD detector