

Tellurium Co-Precipitation – Revisited

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Tellurium Co-Precipitation – Revisited

- Historical Background
- Current Methodology
- Research
- Conclusions

BASF

Tellurium Collection Method: Historical Background

- **Spectrophotometric determination of traces of palladium after coprecipitation with tellurium**
- By: Eliot R.R. Marhenke, E.B. Sandell
- Analytica Chimica Acta, Vol. 28, 1963, Pg 259-263
- School of Chemistry, University of Minnesota

Abstract

A spectrophotometric method for the determination of microgram amounts of palladium in the presence of much iron, copper, nickel, cobalt and other common elements (~ 0.5 g) is described. Palladium is separated by stannous chloride precipitation with tellurium as collector. *p*-Nitroso-diphenylamine is used as the colorimetric reagent, and diethyl oxalate as extradant for the palladium complex (sensitivity = 0.0015 $\mu\text{g Pd cm}^{-2} \equiv \log \{I_0/I\} = 0.001$). Silver, selenium and tungsten lead to low results and should not exceed ~ 0.1 mg. The weight ratio Au/Pd should not exceed 10, else results for palladium are high. For Pd > 1 μg , recoveries average 90% or. better.

Tellurium Collection Method: Historical Background

- Based on analysis of geological samples
 - Fire assay often was used concentrate PM in sample to allow larger sample size
- Allowed for different types of detection after precipitation
 - Colorimetric
 - Thermal neutron activation
 - AAS
 - ICP-OES or ICP-MS
- Determination of precious metals in ore and rocks by thermal neutron activation/spectrometry after preconcentration by nickel sulphide fire assay and coprecipitation with tellurium, *Anal. Chim. Acta.*, 196, 49-58, 1987
- Determination of the precious metals in geological materials by inductively coupled plasma-mass spectrometry (ICP-MS) with nickel sulphide fire-assay collection and tellurium coprecipitation, *Chemical Geology*, 83, 199-132, 1990
- Extraction-back extraction preconcentration in the system based on p-alkylaniline and oil sulfides for determining platinum-group metals and gold by inductively coupled Plasma atomic emission spectrometry *J of Anal Chem*, 64, 877-885, 2009



Tellurium Collection Method: Historical Background

- Current BASF method was adapted from a Japanese method by Shenouda in early 1990s
- Official method was presented at International Precious Metals Institute Conference in 2002
 - Fast turnaround time
 - Less labor intensive
 - Excellent collection of Platinum, Palladium and Rhodium
 - Applicable to a wide variety of sample types including metal monolith
 - Reduced lead usage in the Fire Assay Section

Standard Methodology: Tellurium Collection / ICP-OES

The sample is fused with Na_2O_2 , and the melt is dissolved in hot deionized water, acidified with HCl.

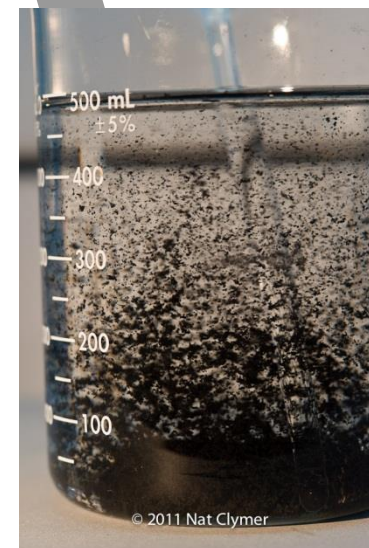
- Peroxide will oxidize metals to metal oxides which allows them to be soluble.
- Hydrochloric acid is used to convert metal oxides to metal chlorides to make water soluble
- Fluoroboric acid is used to keep silicates in solution by stopping polymerization



Standard Methodology: Tellurium Collection / ICP-OES

Solutions of Te^{4+} and Sn^{2+} are added to acidified solution and flocculated.

Pt, Pd and Rh are co-precipitated quantitatively with Te and filtered leaving the interferences in solution

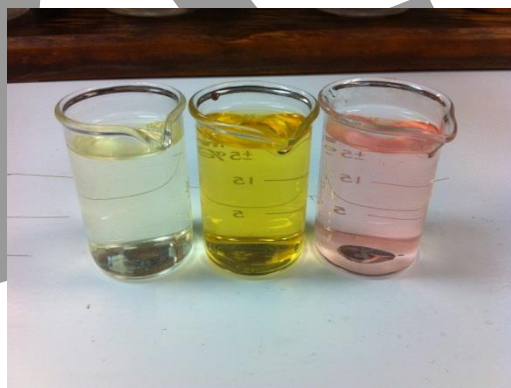


Standard Methodology: Tellurium Collection / ICP-OES

The precious metals and Te are dissolved in aqua regia and the Pt, Pd and Rh may then be measured by ICP-OES.

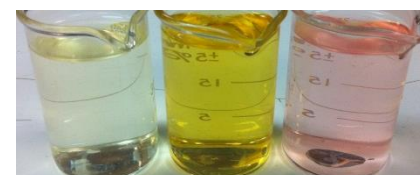
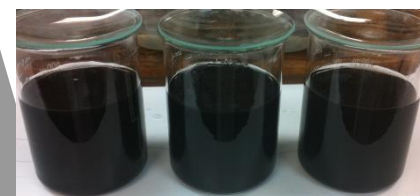
By applying the tellurium collection method, the sample solution matrix consistency is improved, and the complexity of the matrix is reduced.

Method accuracy is $\pm 2\%$; Analysis time is 2-5 days.



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Precious Metal Assay Services



■ Understand/verify fundamental chemistry

■ Is there a way to improve this method:

■ Can we make it faster?

- Can we use less reagents?
- Are there other reagents that could be used?

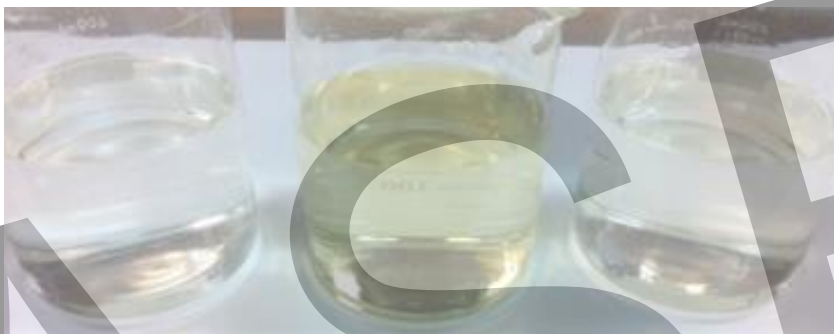
PM-Tin Chemistry

Acidified solution

Pt

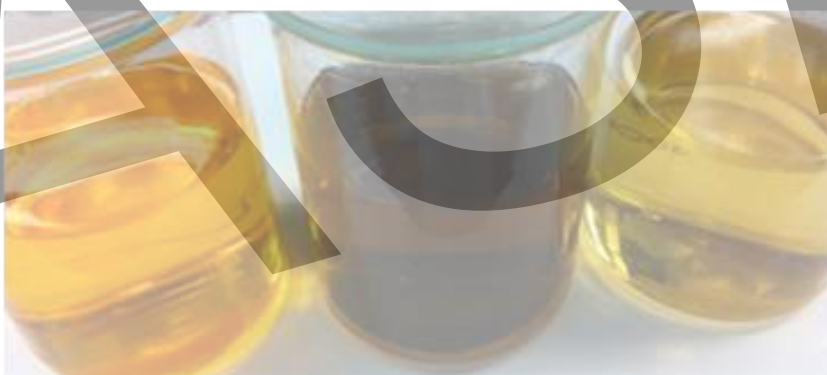
Pd

Rh



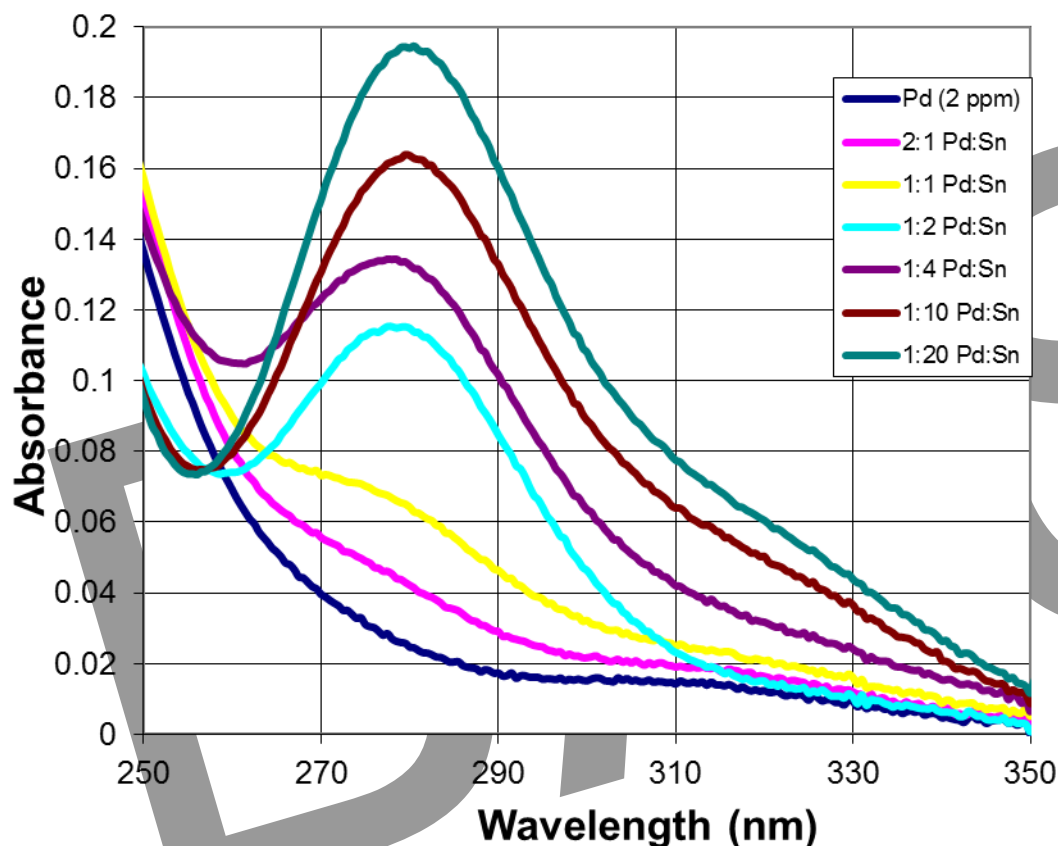
**After addition of
Sn²⁺ solution**

(Sn²⁺ solution is
clear/colorless)



Precious Metal - Tin chemistry

Palladium with Tin

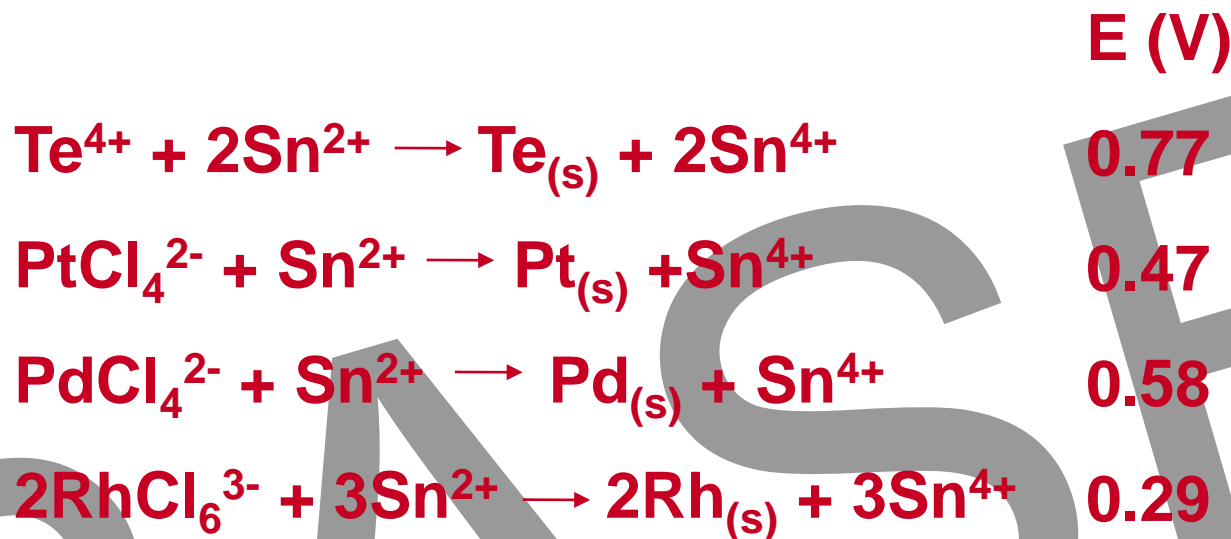


■ Complexation is known to occur in the platinum group metal

■ Absorption of complexes once used to determine PM concentration

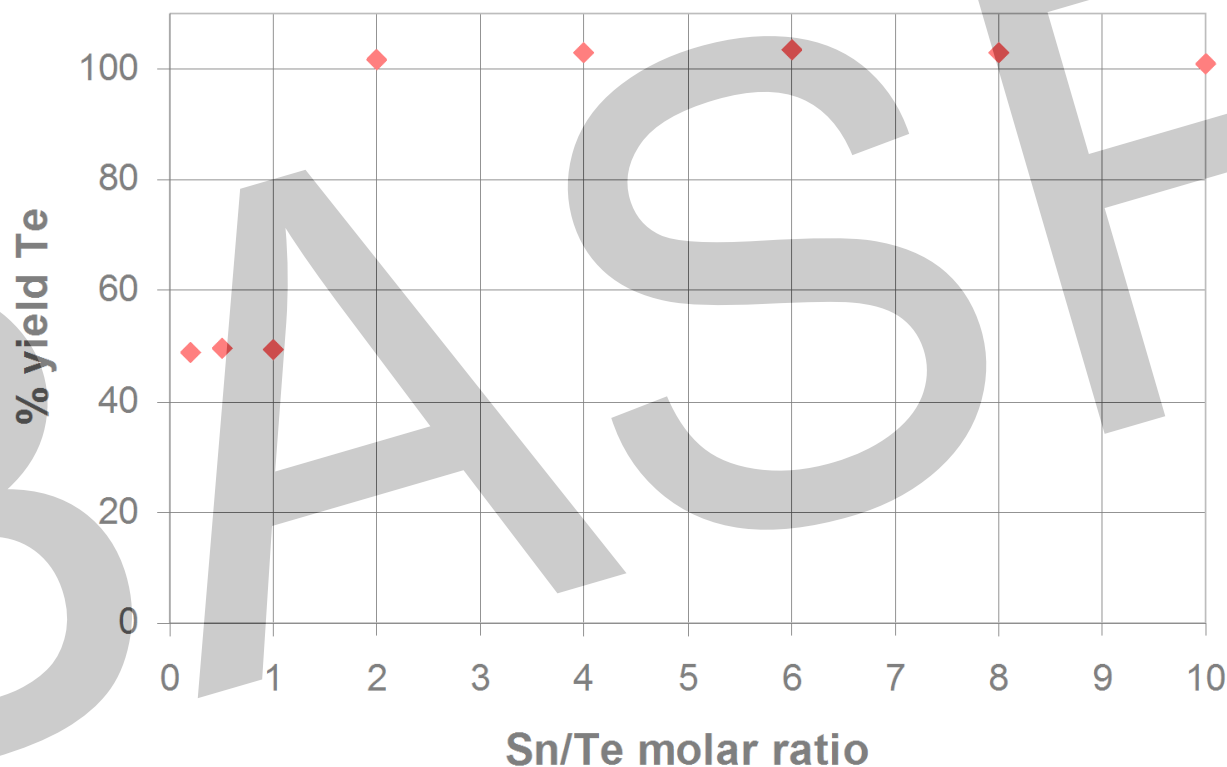
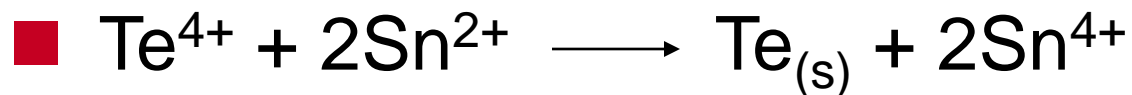
■ Structures thought to be:
 $[\text{Pd}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$
 $[\text{Pt}_2\text{Cl}_2(\text{SnCl}_3)_2]^{2-}$
 $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4-}$

Proposed Reactions:

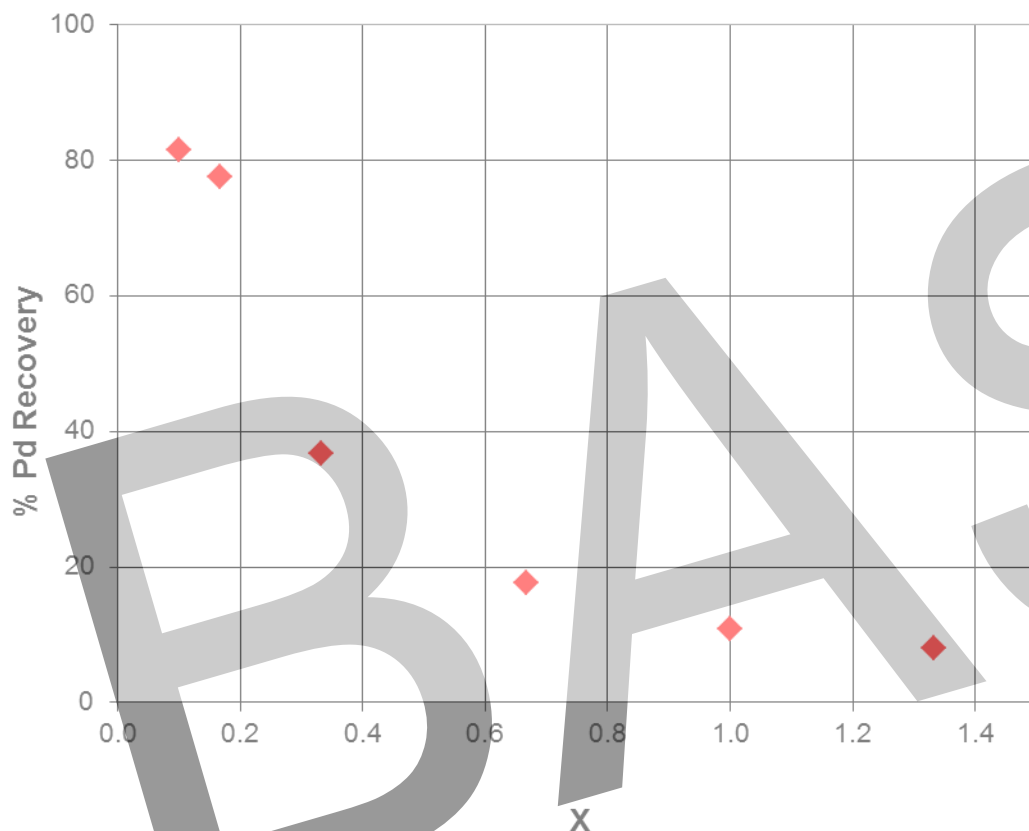


- Both Sn and Te are needed to precipitate PM
 - Adding just Sn or Te to PM will not cause a reaction
- How much PM can be recovered with a 2:1 Sn:Te molar ratio?

Gravimetric verification of Tin/Tellurium Reaction



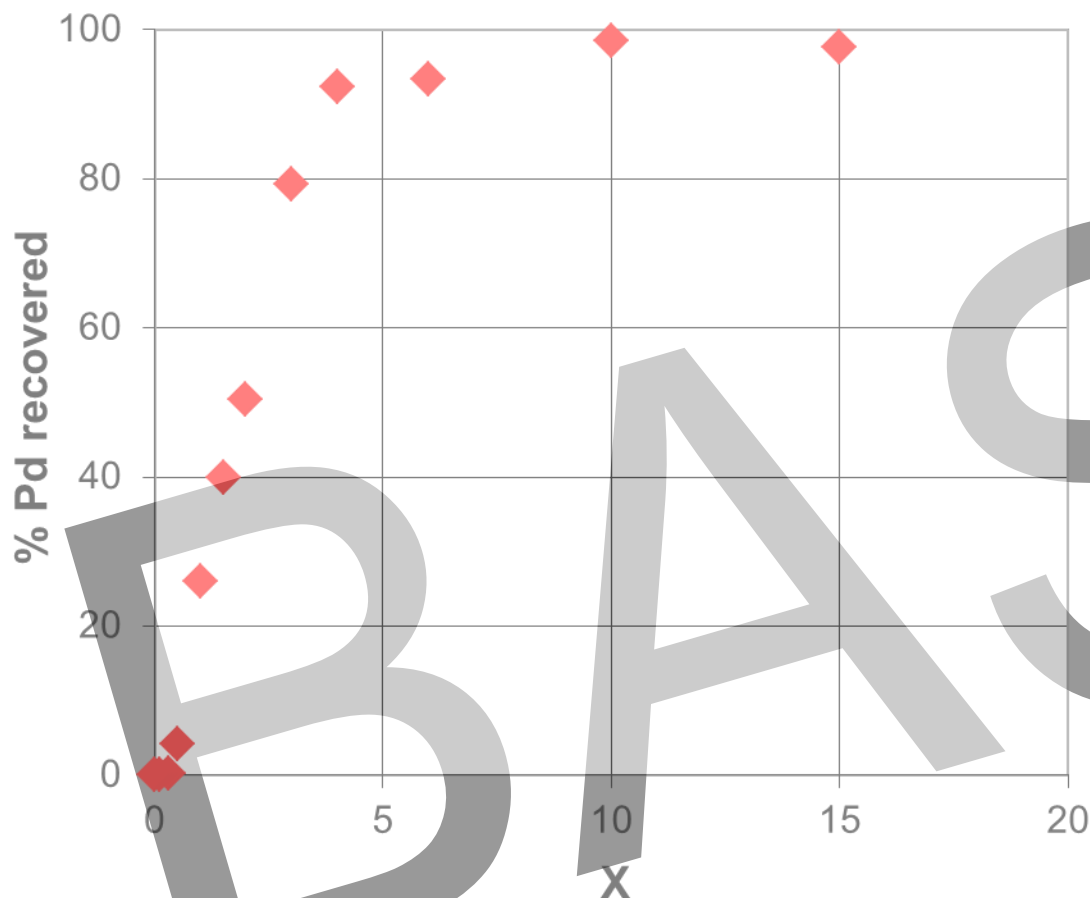
How much PM can be precipitated, given a 2:1 molar ratio of Sn:Te?



- Pd system shown
- Pt and Rh show a similar trend
- Pt:Sn:Te = 0.2:2:1 for 100% Pt recovery
- Rh:Sn:Te = 0.2:2:1 for 100% Rh recovery

Molar ratio of Pd:Sn:Te = X:2:1

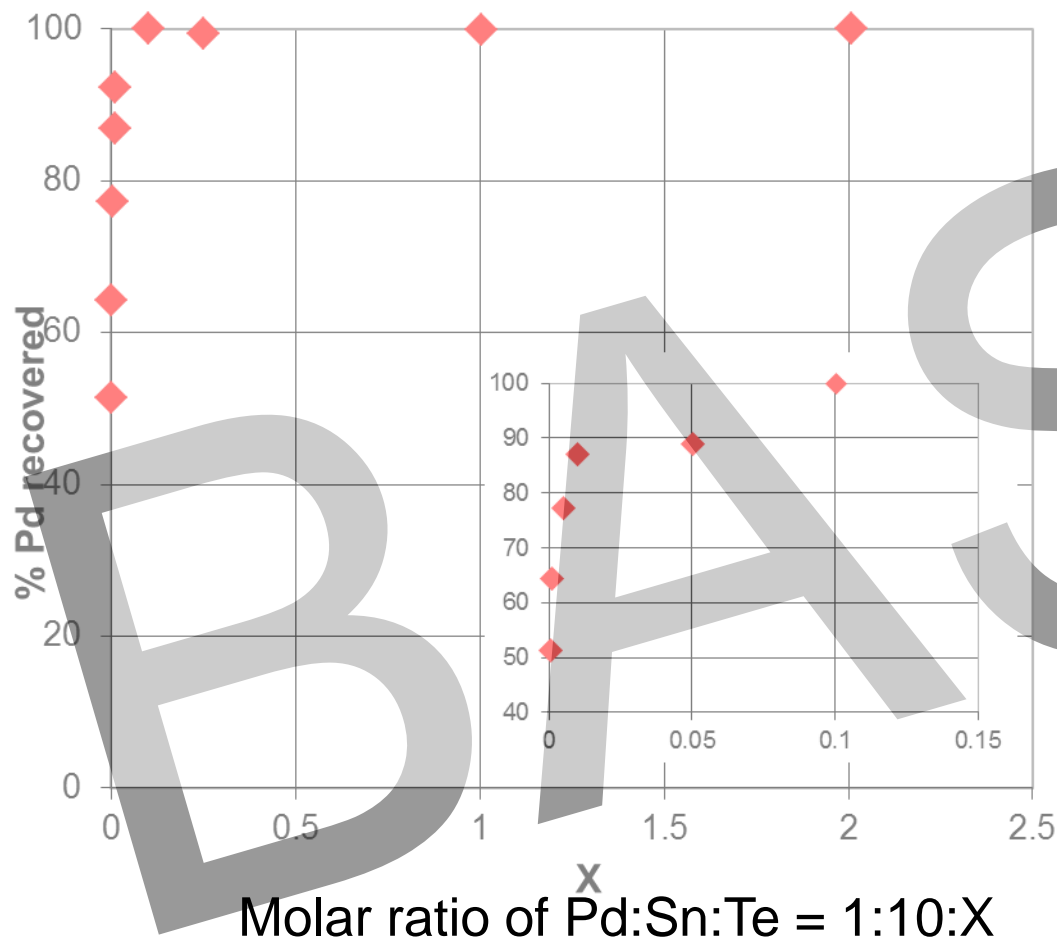
Amount of Sn Needed



Molar ratio of Pd:Sn:Te = 1:X:5

- Agrees with previous experiment
- Pt and Rh show a similar trend
- Pt:Sn:Te = 1:12:5 for 100% Pt recovery
- Rh:Sn:Te = 1:14:5 for 100% Rh recovery

Amount of Te Needed

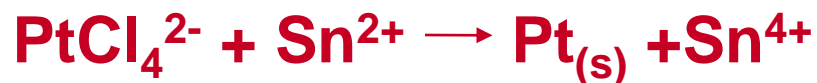


- Agrees with previous experiment
- Pt shows a similar trend
- Pt:Sn:Te = 1:20:0.2 for 100% Pt recovery
- More tests need to be run on the Rh system

In typical method

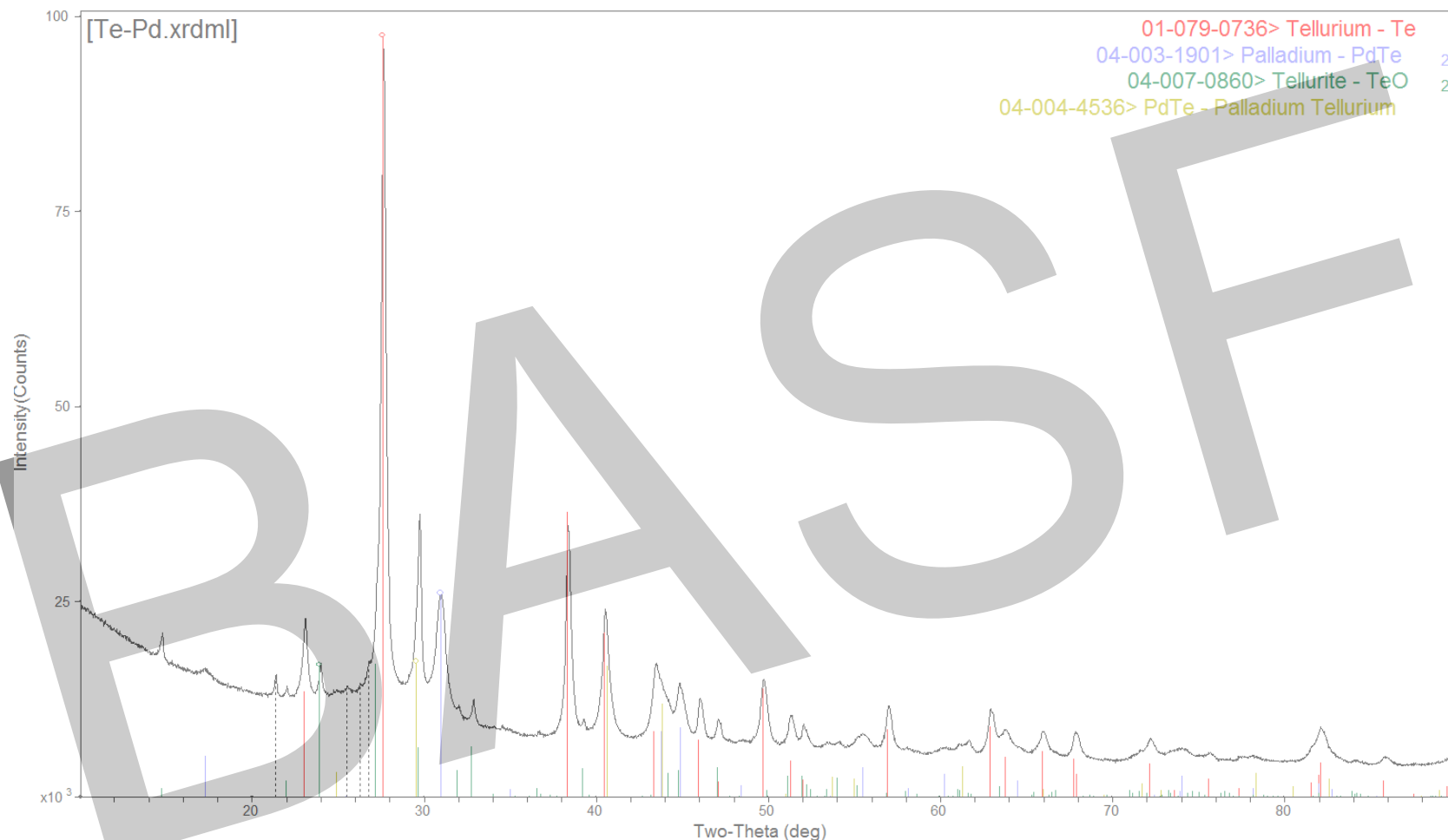
- Ratio of PM:Sn:Te is 1:70:4 (if sample has 1% Pt, Pd and Rh)
- Gross excess of Sn used in method
- Experiments show that amount of tin may be decreased
- What are we making in redox reactions?

Can we identify the products of the redox reaction?



- X-Ray Diffraction for crystal structure (Iselin)
- XPS for oxidation states of surface atoms (Iselin)
- X-Ray Absorption Near Edge Spectroscopy for oxidation states of bulk samples (LSU)

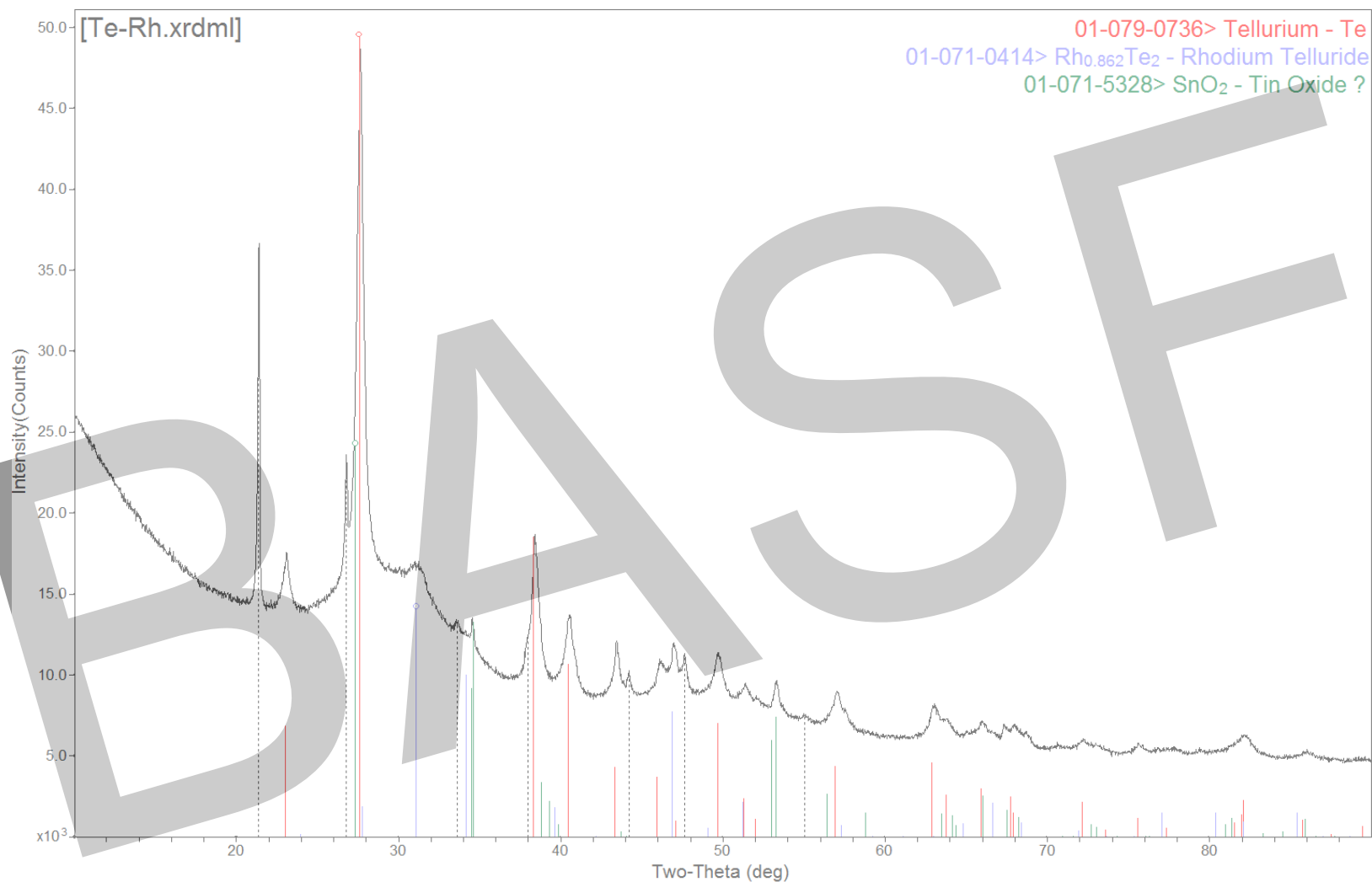
X-Ray Diffraction of Pd sample with Sn and Te



X-Ray Diffraction of Pt sample with Sn and Te



X-Ray Diffraction of Rh sample with Sn and Te



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XPS Data Summary Table

	Pd-Te	Rh-Te	Pt-Te
Surface Composition Table (Atom %)			
Element/ID ¹			
C CHx + COx	18.8	13.4	4.0
Cl chloride	1.0	4.7	1.2
O	40.4	31.9	48.3
Pd Pd ⁺²	1.2		
Pd Pd ⁺⁴	0.3		
Sn SnO, SnO ₂	0.8	1.5	3.9
Te Te ⁰	8.5	15.6	4.7
Te Te ⁺²⁻³	1.4	3.8	2.4
Te Te ⁺⁴	27.6	23.5	31.6
Rh Rh ⁰		5.0	
Rh Rh ⁺³		0.68	
Pt Pt ⁰			1.2
Pt Pt ⁺²			2.7

■ XPS was a first attempt at finding the oxidation states of the metals

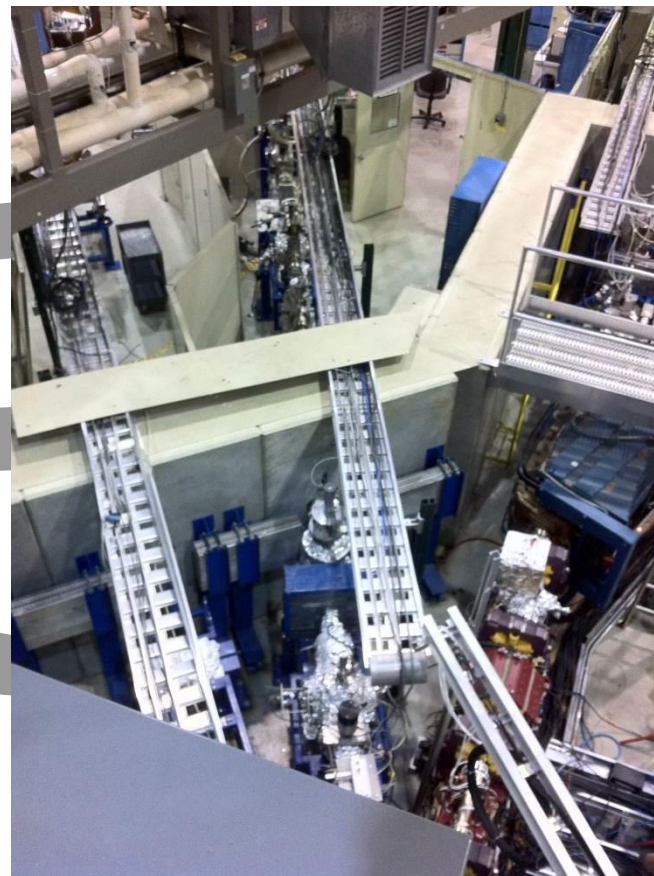
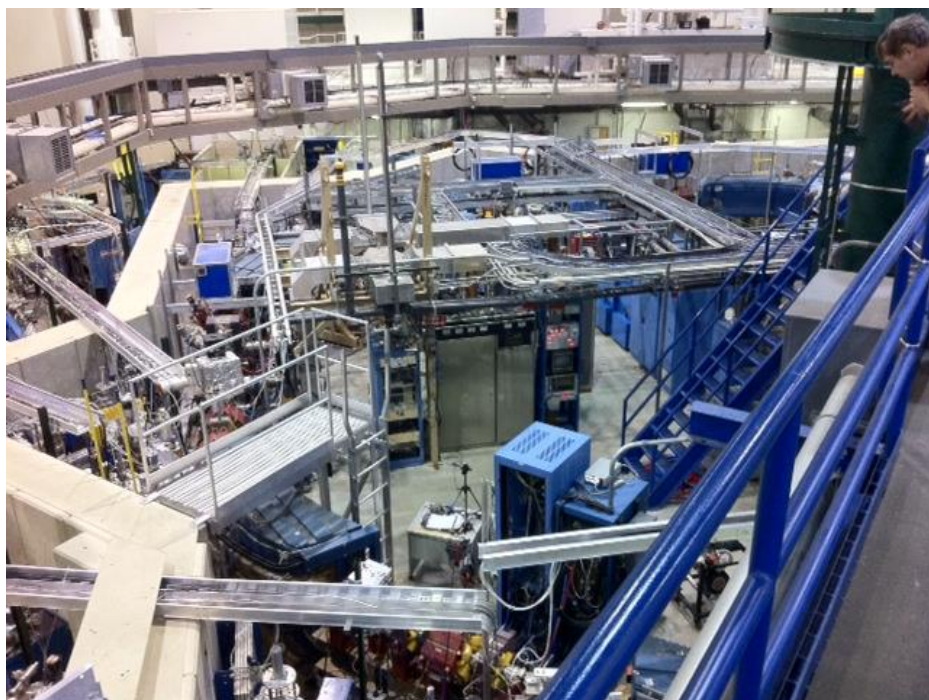
■ All PM and Te had mixed oxidation states

■ Some Sn was left in the product

Issue: XPS is a surface sensitive technique so another method was needed to verify results

Synchrotron at LSU CAMD

BASF in Louisiana had established a collaboration with the X-Ray group



CAMD

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CENTER FOR ADVANCED MICROSTRUCTURES & DEVICES

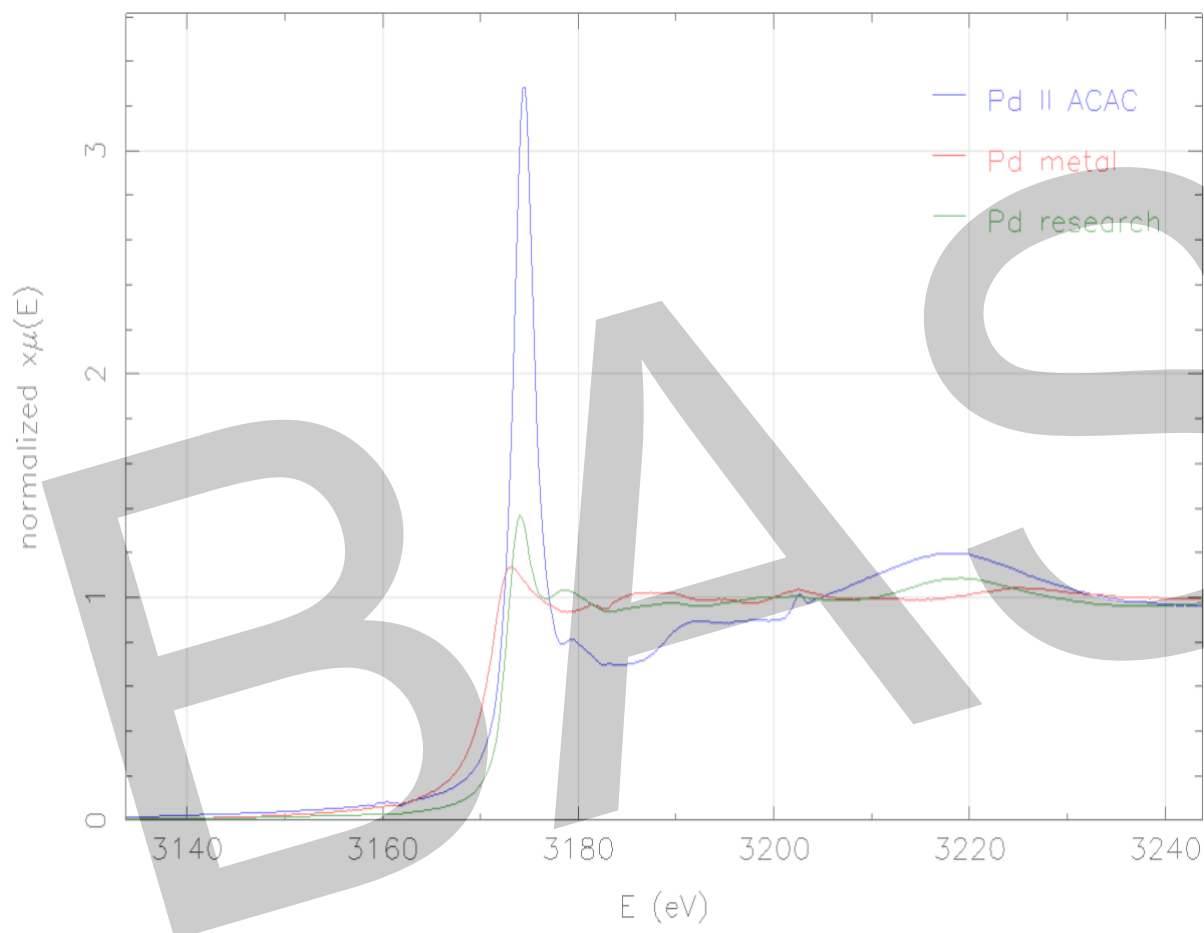
What is XANES?

- Type of X-ray absorption spectroscopy
- X-Ray Absorption Near Edge Spectroscopy – Only extends to about 150eV after absorption edge
- Intense tunable source of soft x-rays is needed only found at synchrotrons
- Can be run in fluorescence or transmission
- Can find oxidation states of atoms, coordination states and geometrical distortions

XANES Experimental conditions

- Following data uses a ratio of PM:Sn:Te of 1:5:1
 - ▶ Need to have enough PM to be seen
- Edges used:
 - ▶ Pd L3– 3175 eV
 - ▶ Pt L3 – 11564 eV
 - ▶ Rh L3 – 3929 eV
- Atmospheres used – Pd needed N₂ atmosphere to counter Ar interference

X-Ray absorption near edge spectroscopy:



- Linear combination of standards gives quantitative results
- 85% Pd⁰
15% Pd²⁺
- 60% Rh⁰
40% Rh³⁺
- 90% Pt⁰
10% Pt²⁺

Summary

- PM not crystalline
- Majority of PM in 0 valent state
- Amount of Sn or Te used for quantitative precipitation is variable depending on experimental conditions
- Current proposed reaction scheme is probable but may not fully explain chemistry
- More research is needed to gain a broader understanding of fundamental chemistry



Future work on project

- Analysis of oxidation states of Te using XANES data needs to be completed.
- EDS Mapping of product
- Order of addition of Sn and Te
- Time scale of reaction – how long does complete PM precipitation take
- Ion chromatography for speciation of PM in solution
- Cyclic voltammetry to evaluate electrochemical properties



We create chemistry