The Separation of Americium from Curium Using New Sodium Bismuthate-based Systems for Used Nuclear Fuel Recycling

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The Nuclear Fuel Cycle

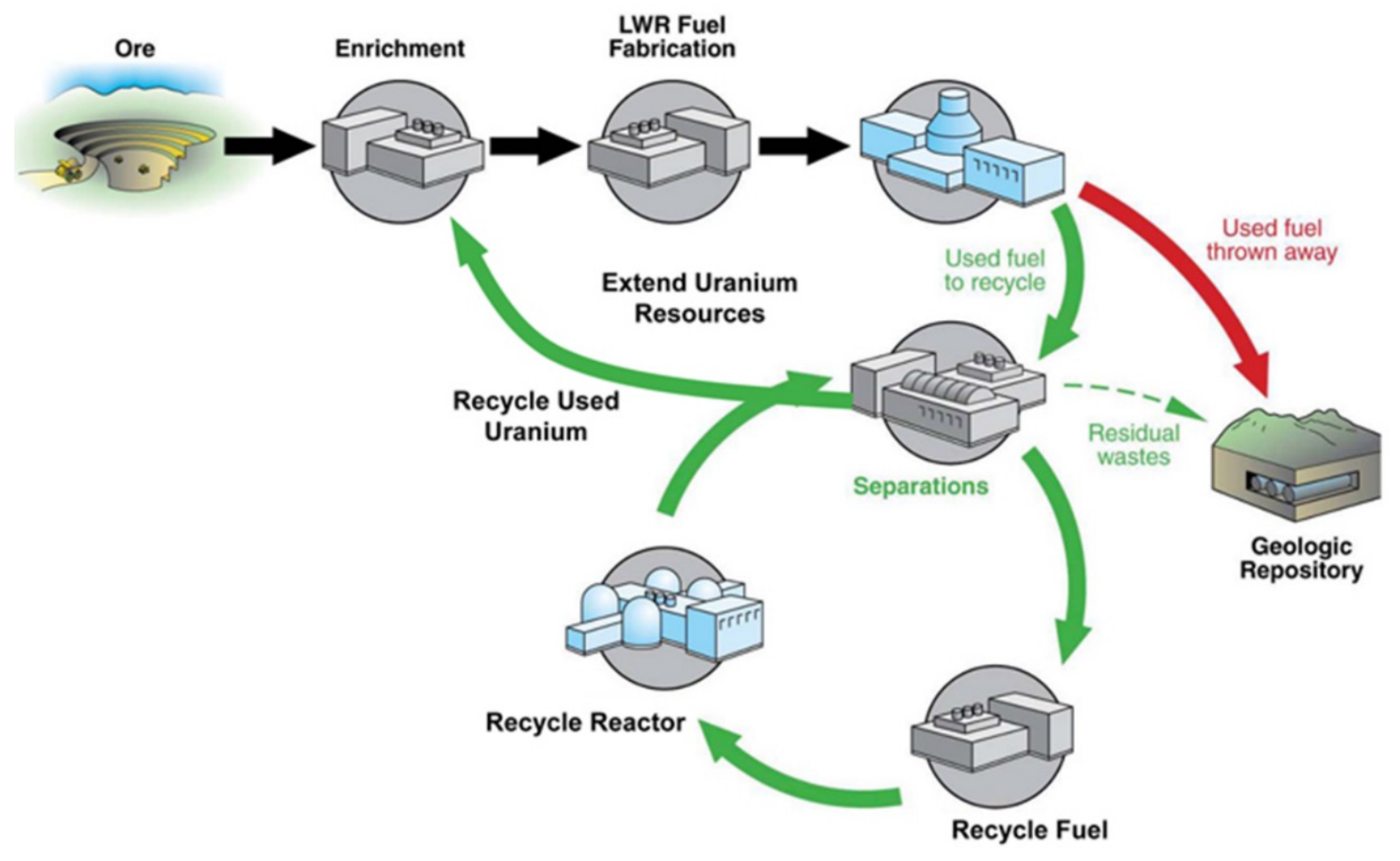


Figure 1: Nuclear Fuel Cycle[1]

- The U.S. currently operates on an "open" fuel cycle generating long-lived radioactive waste
- There are no repositories approved for storage and no long-term storage plan

- Used nuclear fuel contains mainly inert or short-lived elements
- The minor actinides, Am and Cm, have long half-lives that contribute to the long storage time and radiotoxicity of waste
- The actinides are energy-dense and can be used as nuclear fuel

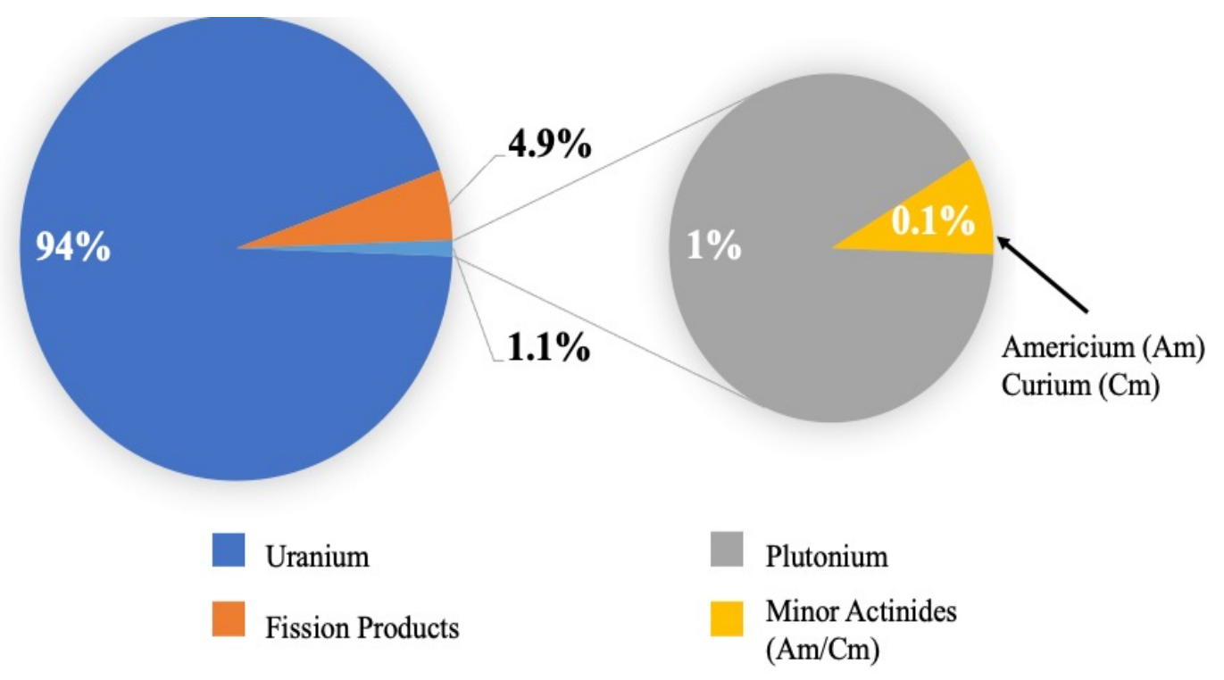


Figure 2: Composition of Used Nuclear Fuel[2]

Partitioning & Transmutation

- "Partitioning" is the separation of radionuclides from used nuclear fuel
- "Transmutation" is the process of using the recovered radionuclides as fuel in nuclear reactors
- P&T decreases the time it takes for the radiotoxicity to reach natural levels from 130,000 years to ~300 years
- P&T decreases the volume, radiotoxicity, and storage time while providing additional clean energy

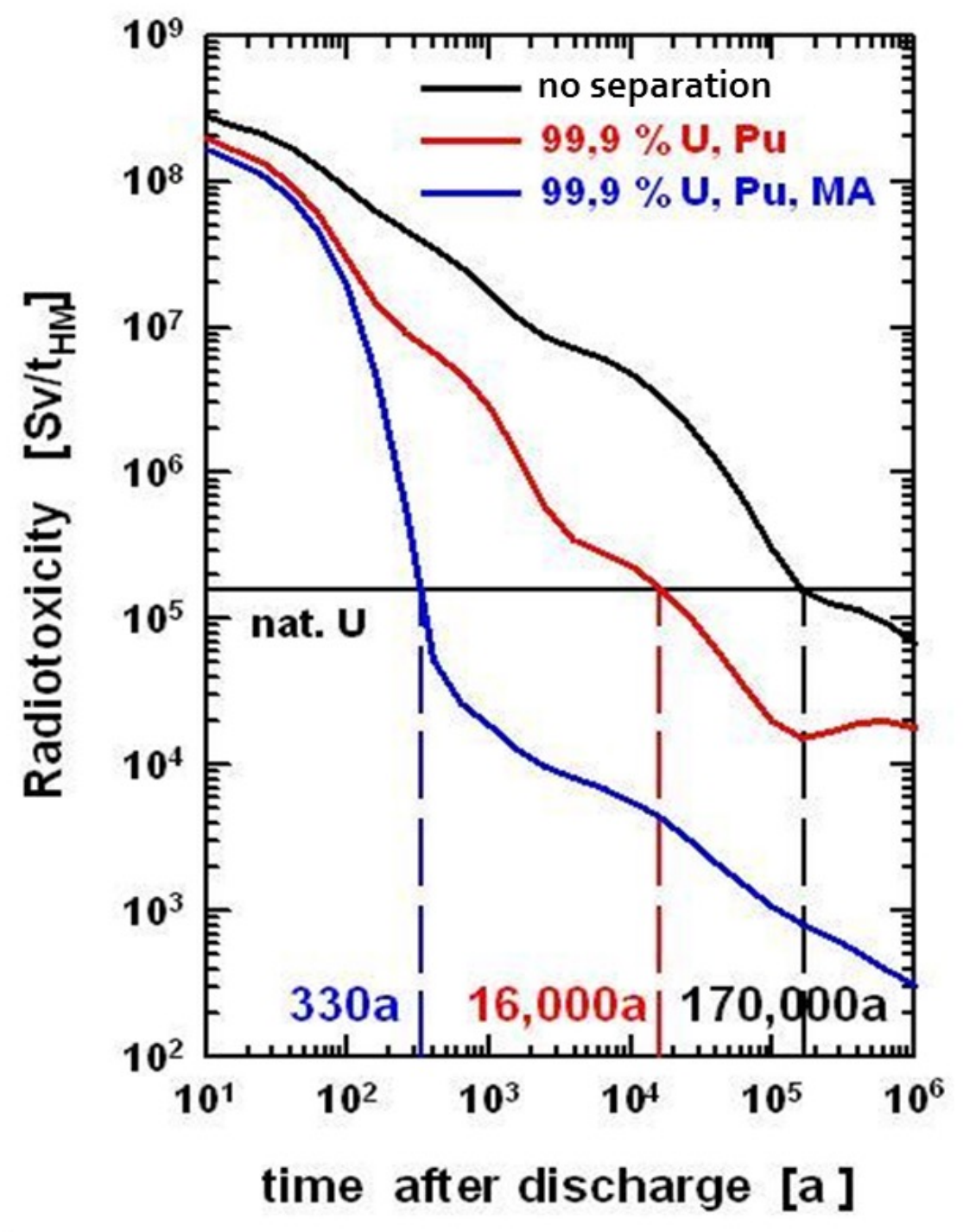
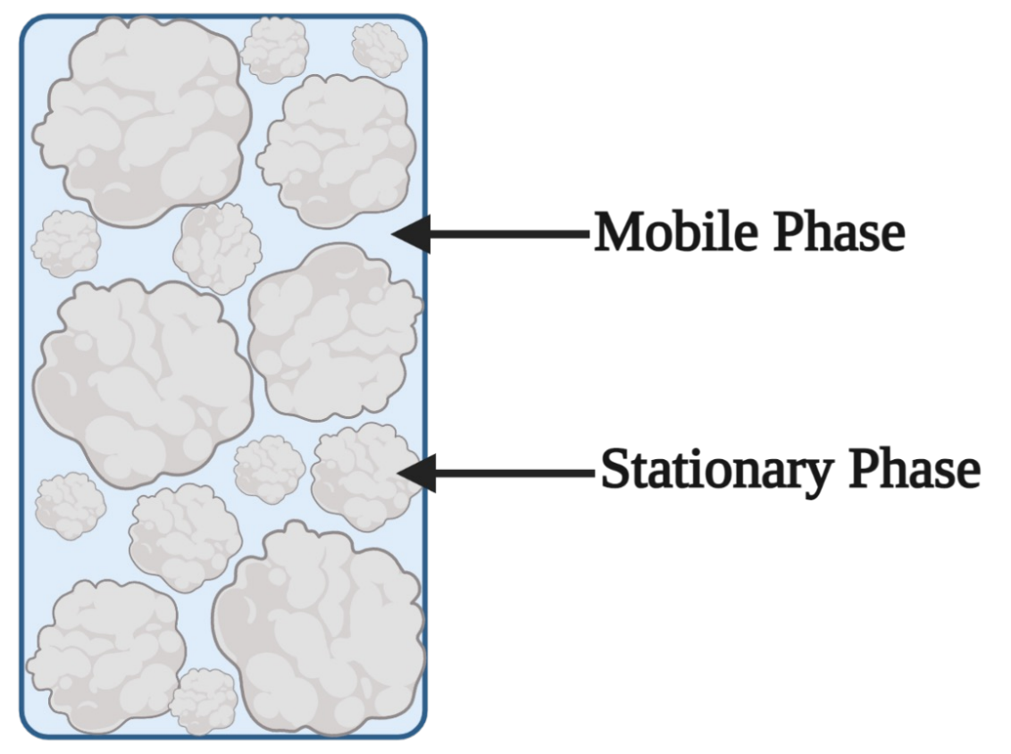


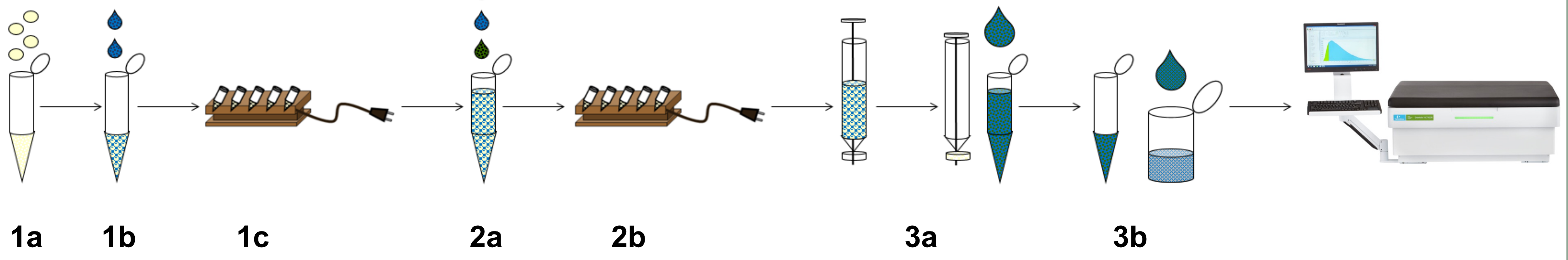
Figure 3: Radiotoxicity Over Time[2]

Solid-Liquid Chromatography



- Chromatographic separation systems have 2 phases
  1. Selective Stationary Phase
  2. Mobile Phase containing analytes of interest
- The stationary phase will adsorb the analytes it is selective for
- Other analytes will remain in the mobile phase and can be collected

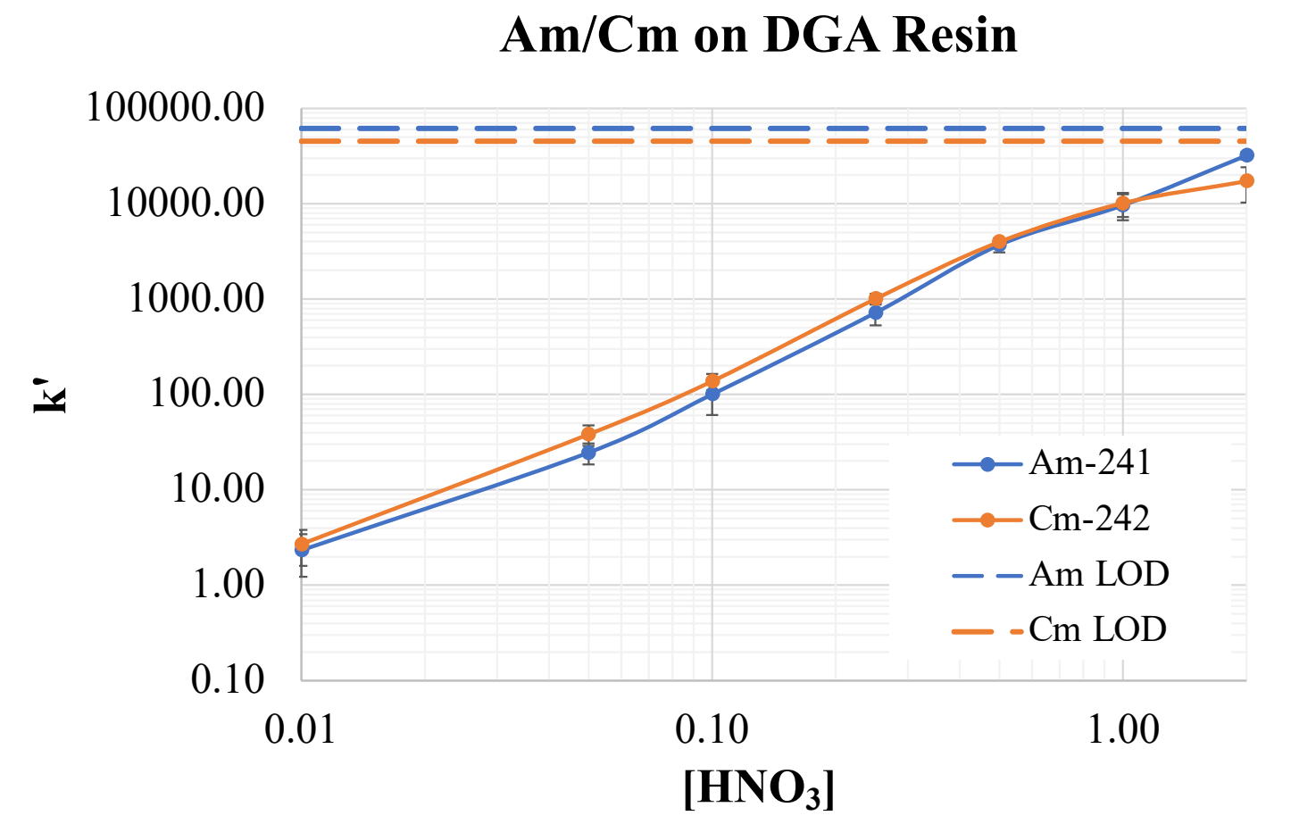
Batch Adsorption Studies



1. **Preconditioning**
   a) 50 mg resin
   b) Desired acid concentration
   c) Agitate for 1 hour
2. **Spiking**
   a) 50 Bq ^{241}Am/^{244}Cm
   b) Agitate for 1 hour
3. **Analysis**
   a) Filter sample using PTFE syringe filter
   b) Transfer aliquot of the filtered eluent for analysis

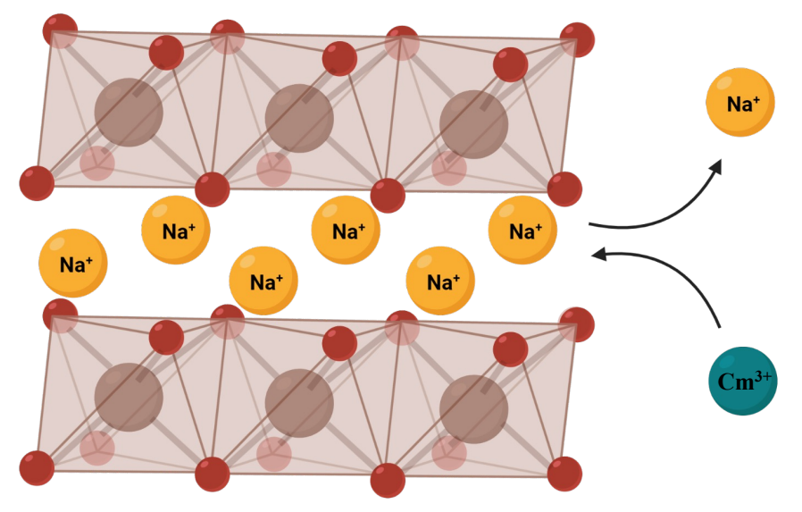
$$D_w = \left(\frac{A_o - A_{aq}}{m_r}\right)\cdot\left(\frac{V_{aq}}{A_{aq}}\right)$$

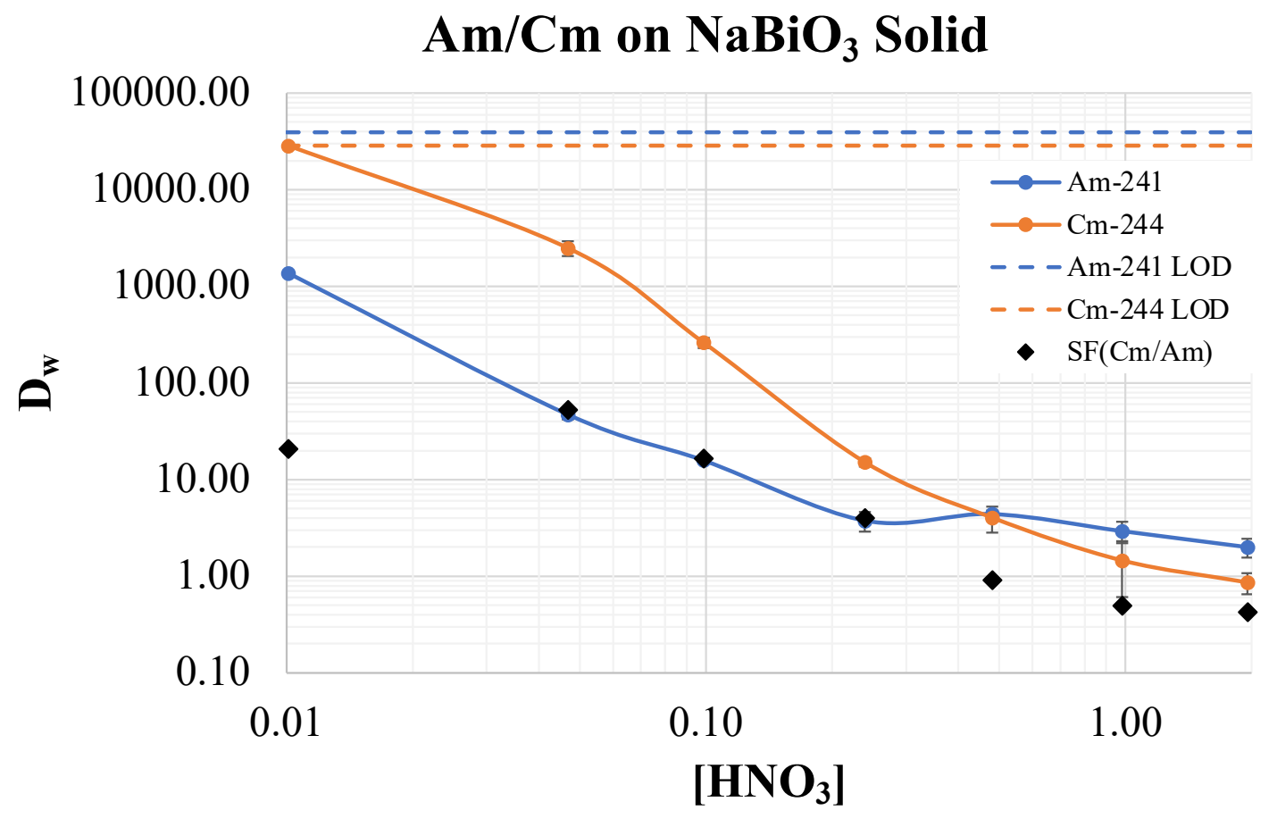
Chemical Behavior of Americium and Curium



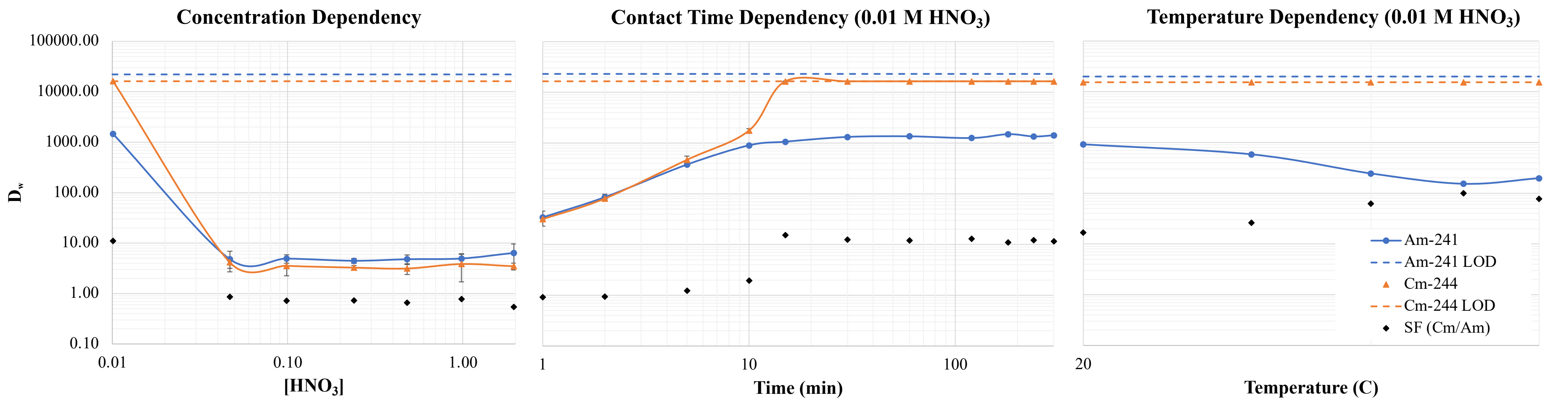
- Am & Cm have ***nearly identical*** behavior in acidic solutions
  - Similar ionic radii/size
  - Similar ionic bonding
  - Similar solubility and precipitation behavior
- **Am & Cm are typically trivalent (+3) in aqueous acidic solutions**

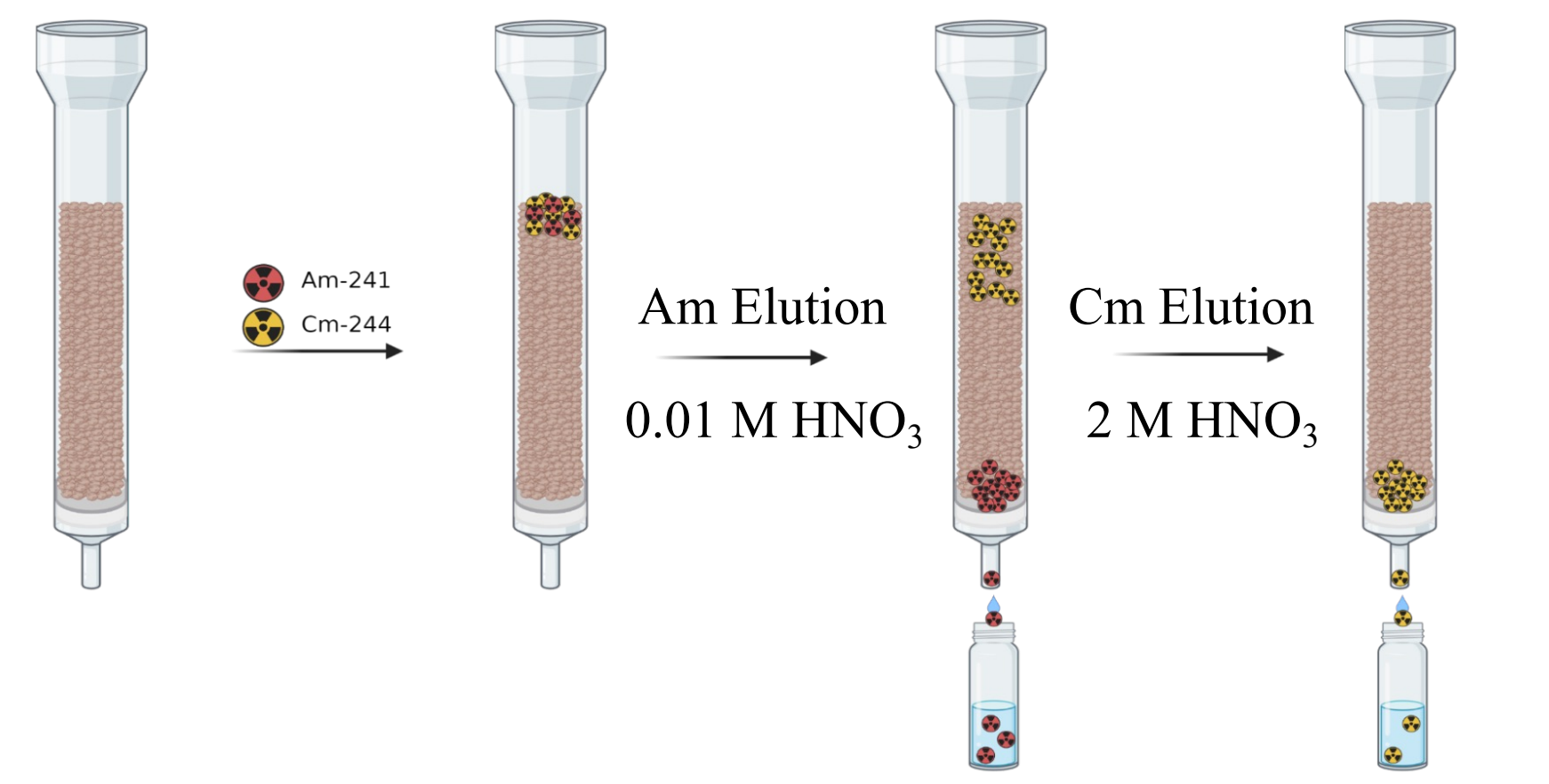
- Cm can not be oxidized in acid
- **Am can be oxidized to +5 and +6 if a strong oxidizing agent is present**
- Sodium Bismuthate ($NaBiO_3$) is a solid oxidizing agent with an ion-exchange structure

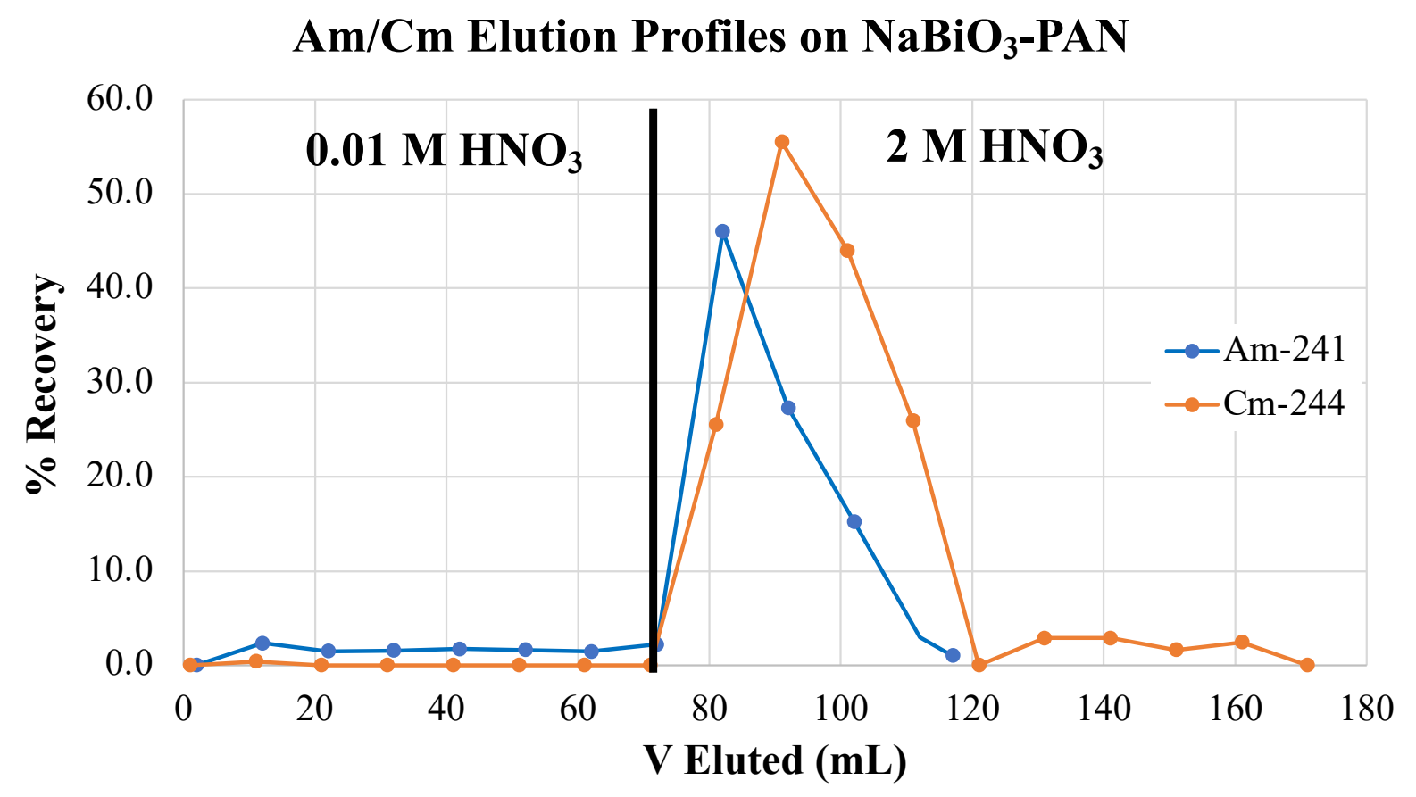




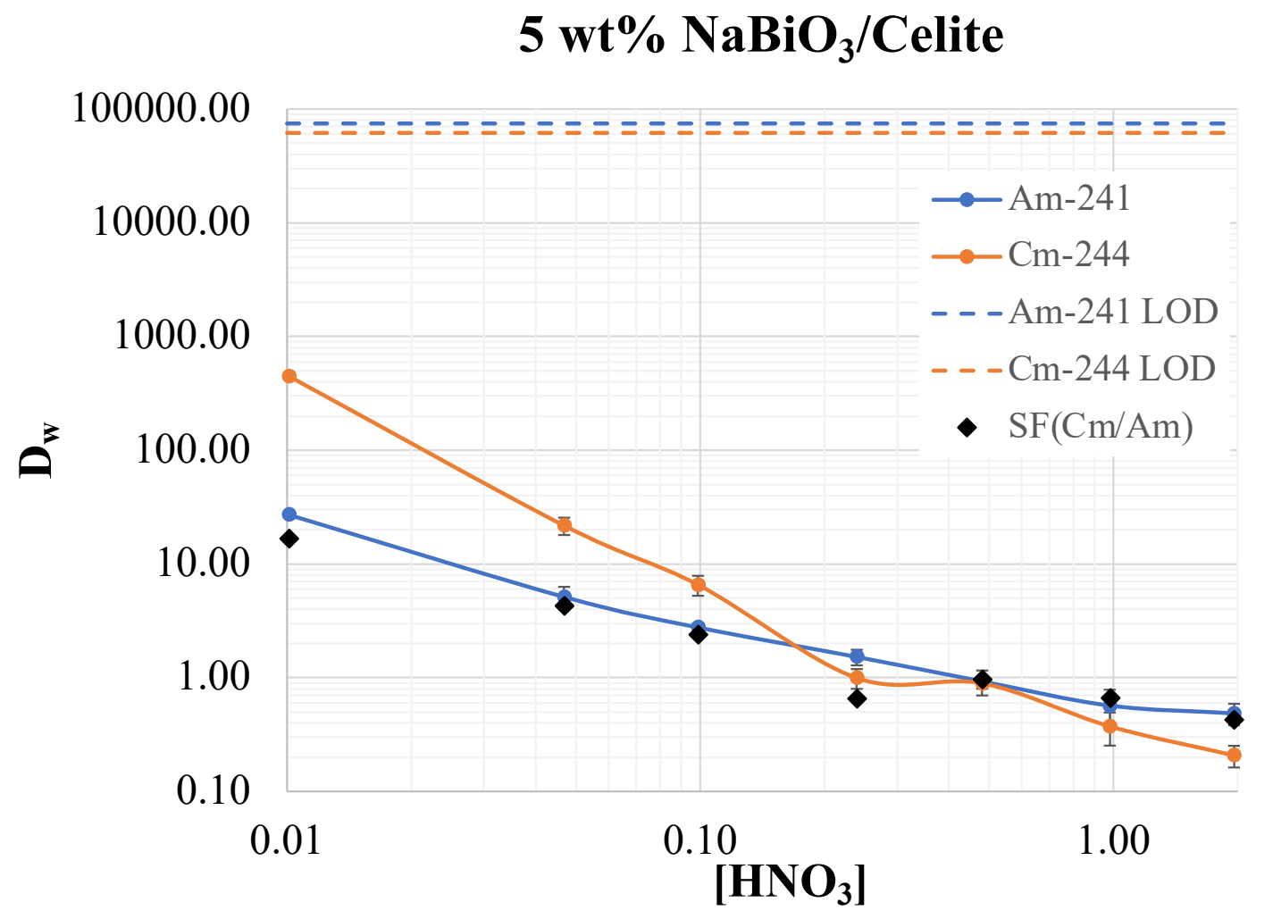
Sodium Bismuthate-Coated Resin by TrisKem Inc.





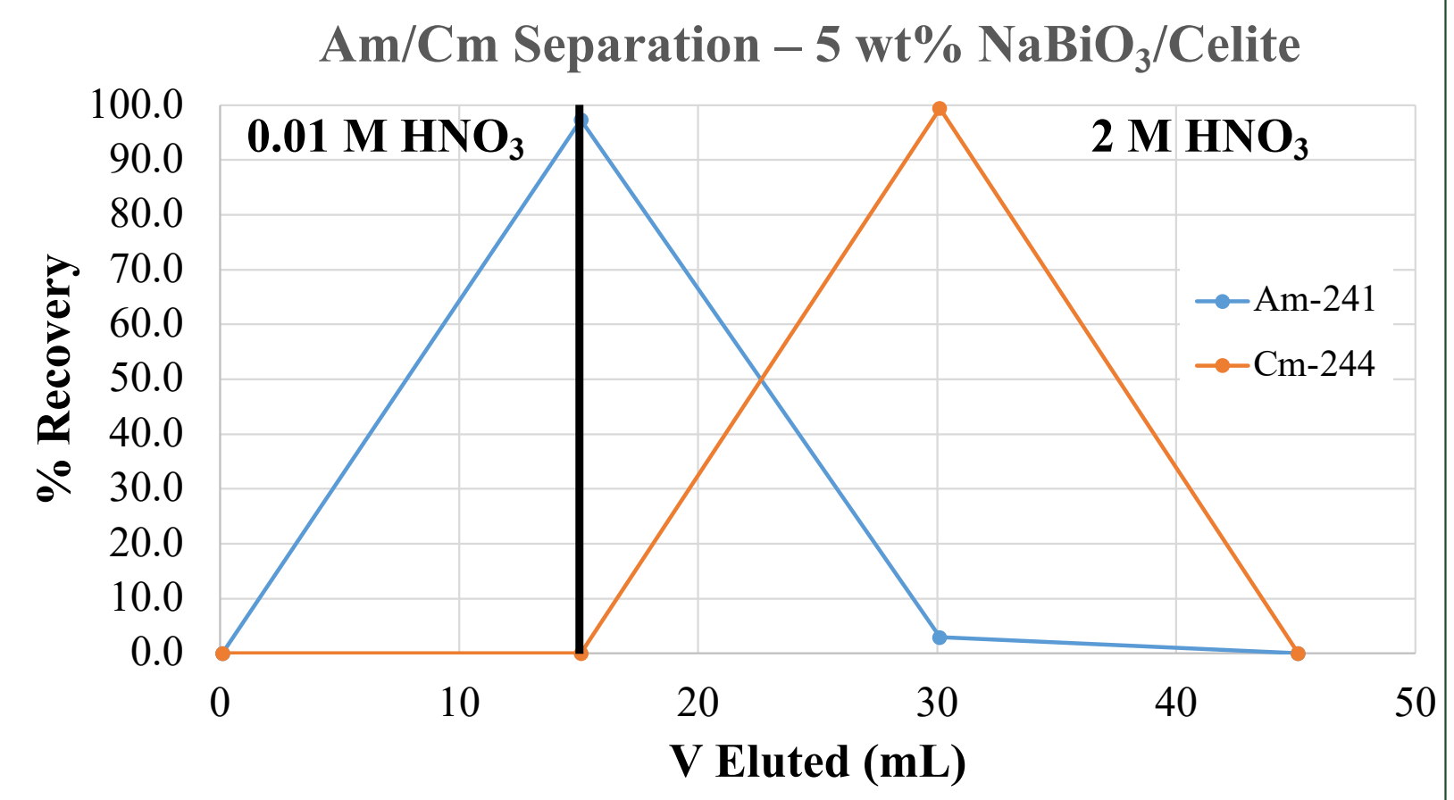


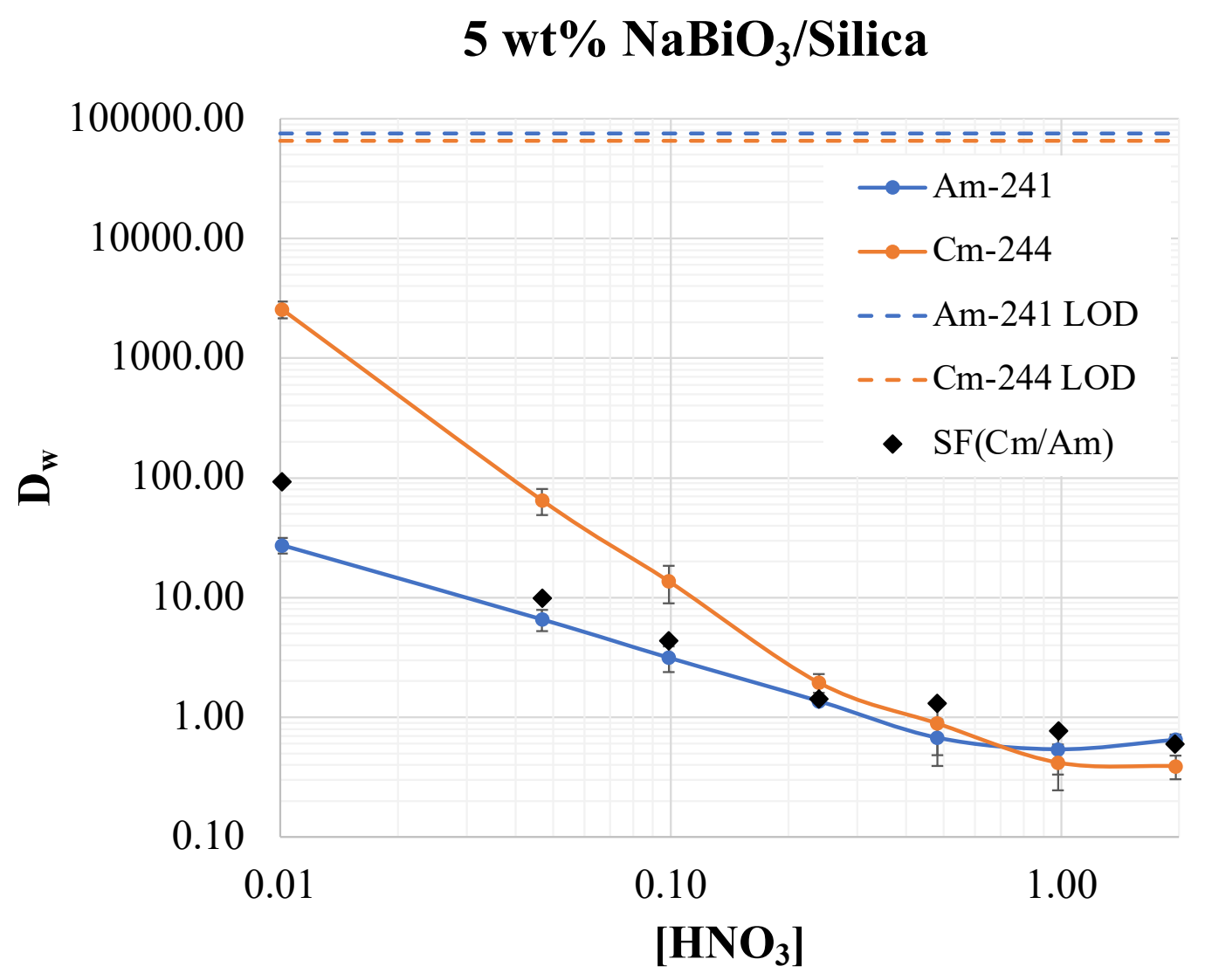
Mixed Bed Chromatographic Systems



5 wt% $NaBiO_3$/Celite	
[HNO_3]	SF (Cm/Am)
0.01	**16.55**
0.05	4.24
0.10	**2.37**
0.24	0.65
0.48	0.96
0.98	0.66
1.96	0.43

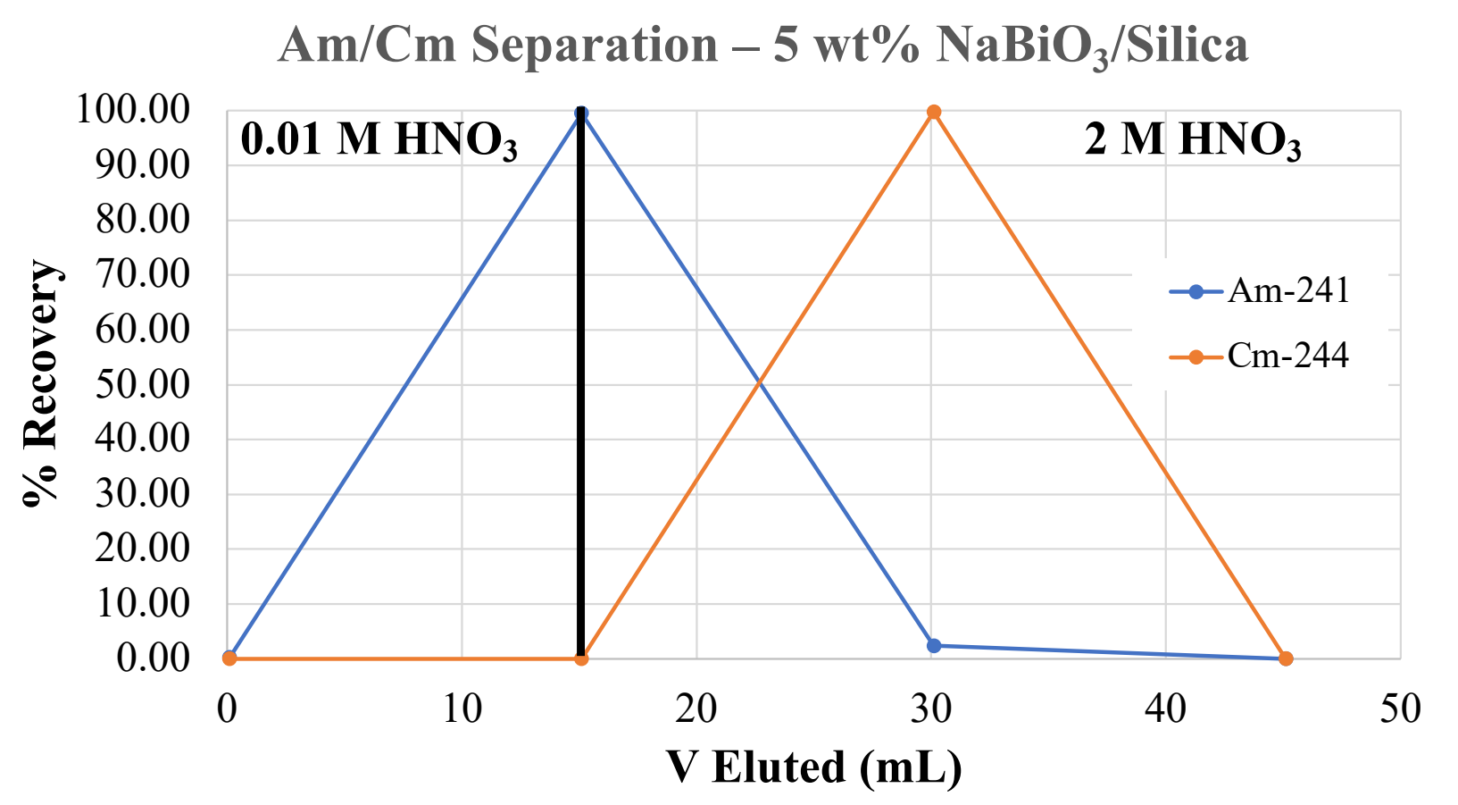
- 98% Am-241 recovery in 0.01 M HNO3
- 100% Cm-244 recovery in 2 M HNO3
- ~2% Am-241 breakthrough in Cm-244 fraction
- Poor flow under gravity





5 wt% $NaBiO_3$/Silica	
[HNO_3]	SF (Cm/Am)
0.01	**93.40**
0.05	9.87
0.10	4.35
0.24	1.43
0.48	1.31
0.98	0.77
1.96	0.60

- 99% Am-241 recovery in 0.01 M HNO3
- 100% Cm-244 recovery in 2 M HNO3
- ~1% Am-241 breakthrough in Cm-244 fraction
- 0.5 mL/min flow under gravity



Next Steps

- Optimize column parameters (flow rate, column height/width, packing method)
- Immobilize $NaBiO_3$ onto inorganic support material

References

1) Argonne National Laboratory, *Pyroprocessing Brochure*, ***2018***
2) IAEA Technical Reports Series #435, *Implications of Partitioning and Transmutation in Nuclear Waste Management*, **2004**.

Acknowledgements

- MAP-ERC
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- Department of Environmental & Radiological Health Sciences

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The Effect of Asphalt Debris on Radiochemical Analysis of Plutonium

Raissa Chunko, Ralf Sudowe

Background

- In case of an incident involving a radiological dispersal device, robust and rapid separation techniques must be available.
- The measurement of alpha emitting radionuclides such as plutonium is very important in determining the hazard to rescue workers and the general public.
- A variety of methods for the determination of plutonium in common matrices such as air, water, and soil are available.
- However, only limited techniques are available to measure Pu in unusual matrices such as steel, concrete and glass and other materials found in in urban debris.
- Previous work in our group focuses on developing methods for the analysis of Pu in steel, concrete, and bone ash.[1-2]
- The goal of this project is to quantify the influence that compounds found in common types of asphalt have on the uptake of plutonium on resins commonly used for the separation procedure.

References

1. McLain, D. R.; Liu, C.; Sudowe, R. (2017) Effects of urban debris material on the extraction chromatographic separation of strontium: Part II: cement and concrete. J Radioanal Nucl Chem. DOI: 10.1007/s10967-017-5609-z.
2. Nguyen, N. T. N.; Sudowe, R. (2019) Effect of Matric Constituents on the Determination of Plutonium and Americium in Bone.
3. Daum, J. K.; Sudowe, R. (2018) Determination of Anthropogenic Radionuclides in Ocean Water Using Extraction Chromatography.

Extraction Chromatography

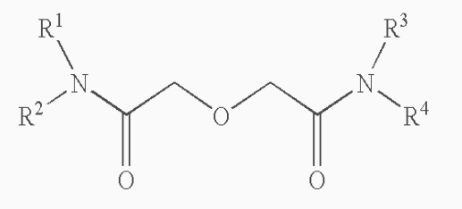
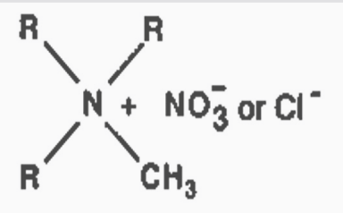
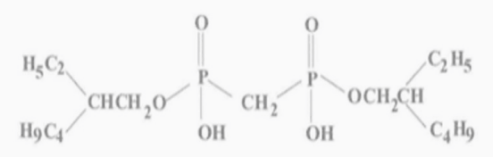
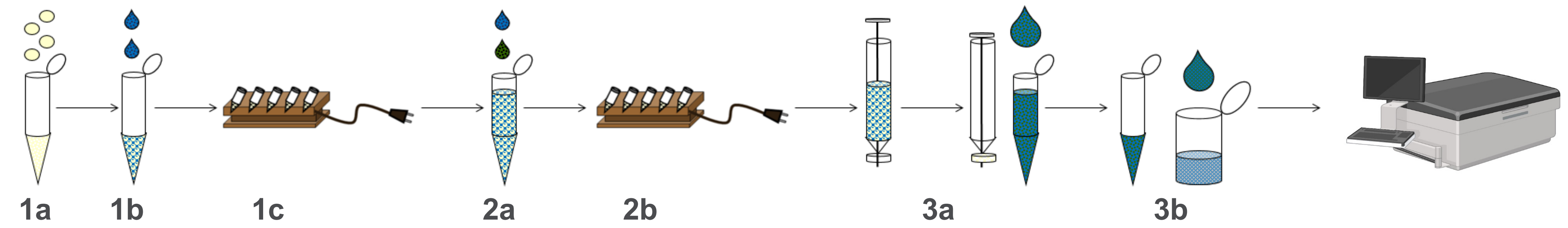
Resin	Extractant System	Acid Concentration (M)	Conversion from D_W to k'
DGA	N, N, N', N' tetraoctyldiglycolamide (TODGA) 	1.0	1.75
UTEVA®	diamyl amylphophonate (DAAP)	3.0	1.67
TEVA®	Aliquat® 336 	3.0	1.90
TRU	octylphenyl-N-N-di-isobutyl carbamoylphoshine oxide (CMPO)	3.0	1.80
Actinide	DIPEX®: bis(2-ethylhexyl) methanediphosphonic acid (H2DEH[MDP]) 	3.0	1.90
Diphonix®	polystyrene/divinylbenzene polymeric support functionalized with diphosphonic and sulphonic acid groups	3.0	2.00

Table 1. Extraction chromatography resins[3]

Method for Uptake Studies



1. **Preconditioning**
   a) 50 mg resin
   b) 0.45 mL acid
   c) Agitate for 1 hour
2. **Spiking**
   a) 1.0 mL calcium solution
   0.05 mL ^{239}Pu (1000 Bq/mL each)
   b) Agitate for 1 hour
3. **Analysis**
   a) Filter sample using PTFE syringe filter
   b) Transfer 0.90 mL aliquot of the filtered eluent into 15.0 mL of LSC cocktail for analysis

Figure 1. Batch study method[3]

Previous Results

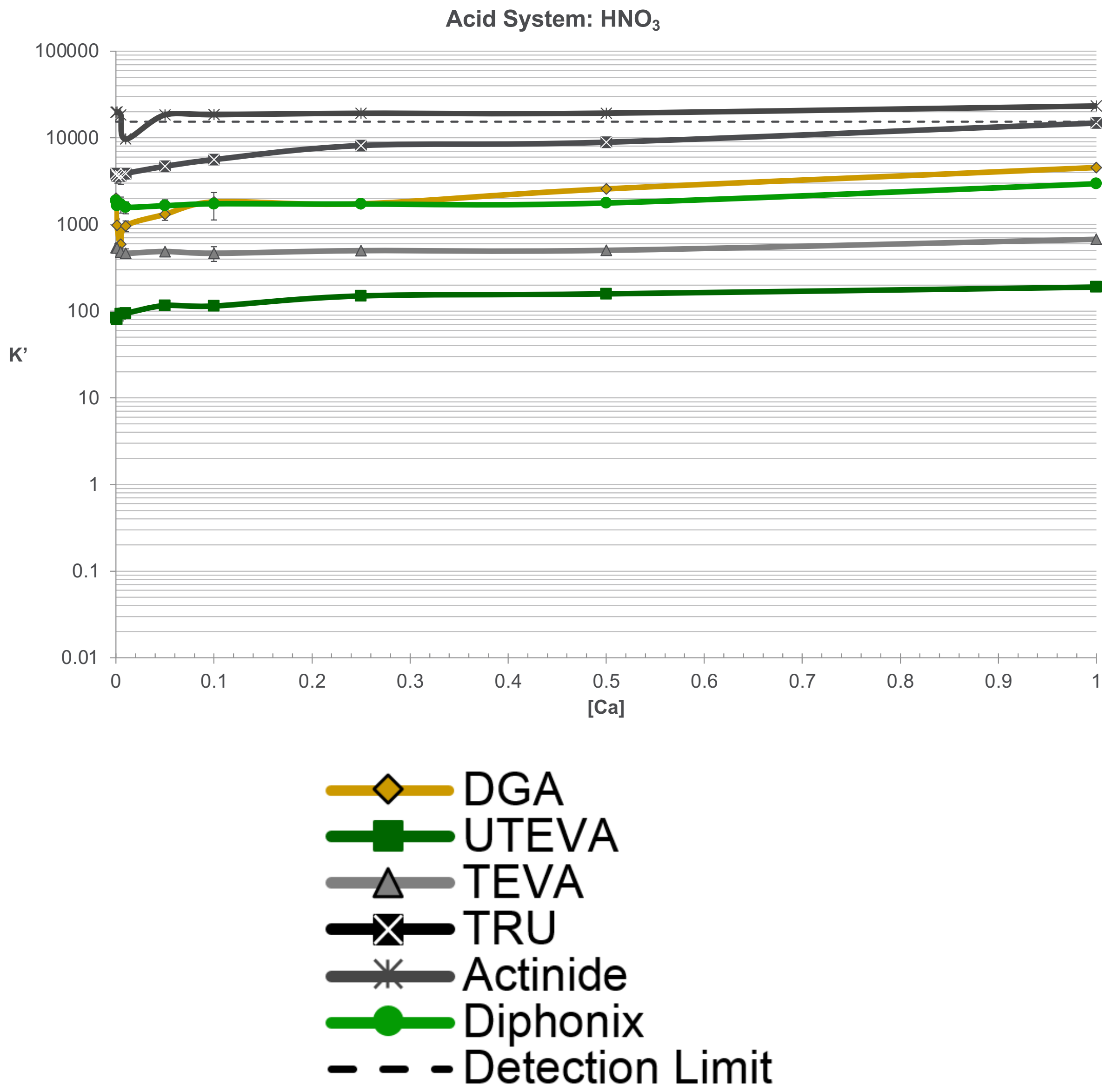


Figure 2. Plutonium retention in presence of calcium[3]

Future Work

- Column studies will be performed to generate an elution profile for Pu in the presence of the interfering ions.
- The effect of the bitumen material used as a binder material on the uptake of plutonium on DGA, TRU, TEVA, and UTEVA resins will be investigated.
- In addition, studies will be conducted to see whether reagents used for sample digestion will interfere with the procedure.

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An Investigative Study of Actinide and Non-Actinide Bearing Fuel Salts

By: Michaella Swinhart

Introduction

The aging United States power grid and energy infrastructure has caused an increase interest in the search for new technologies to produce, transmit, and store energy. With the concern of climate change, security risks, and limited resources for fossil fuels, nuclear reactors are being viewed as the primary source for an emission free energy source for the future. Public interest is growing again in nuclear energy, however, legacy waste from plutonium production and current operating reactors is creating hesitation. Generation IV reactors, such as the Molten Salt Reactor (MSR), are suggested solutions to address these problems. This research entails a detailed exploration into the importance of understanding the thermophysical and chemical properties of actinide and non-actinide bearing fuel and coolant salts for MSR's. These properties are of critical importance to the successful demonstration of MSR's, as they establish essential design constraints.

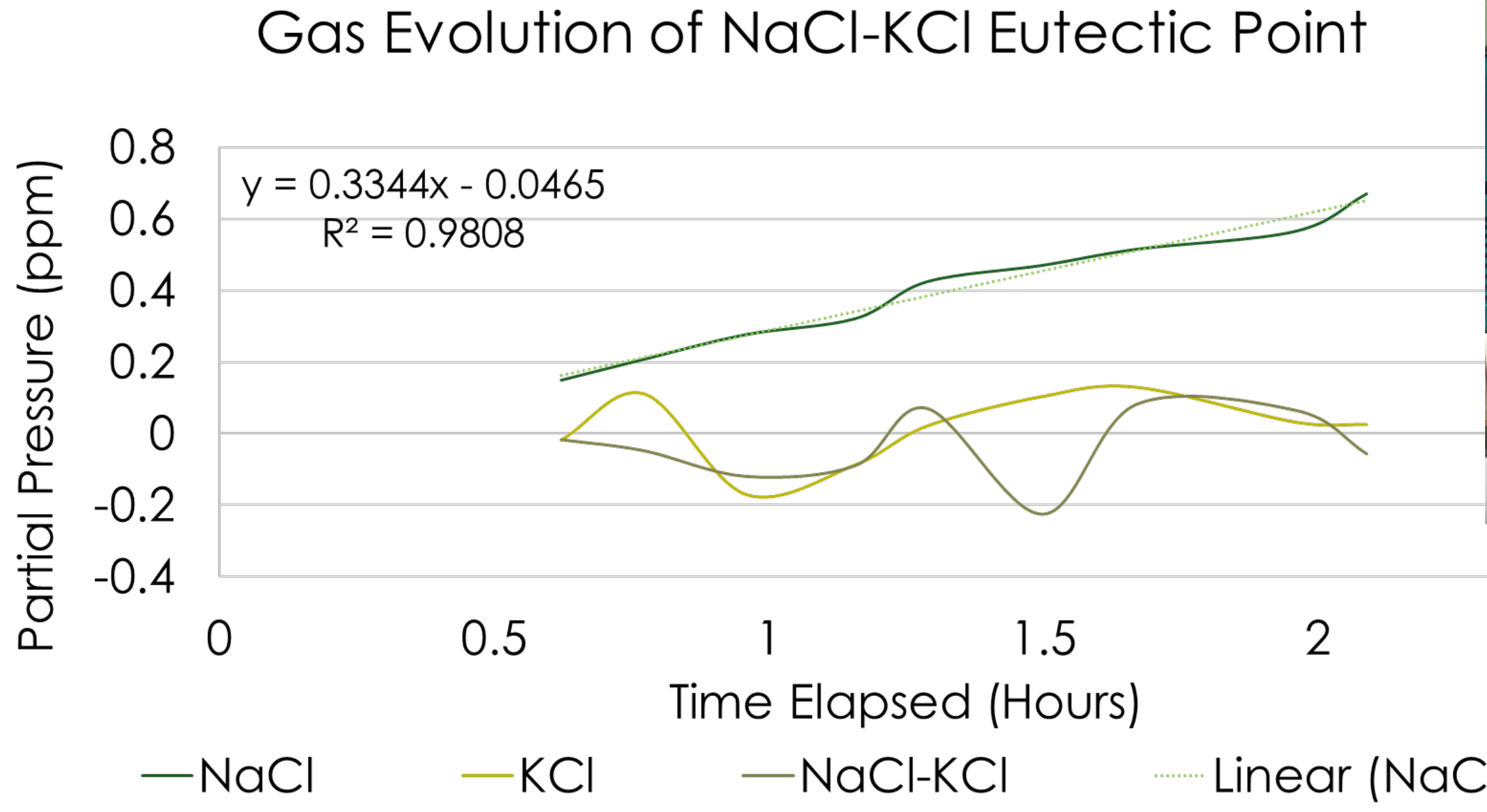
Vapor Pressure

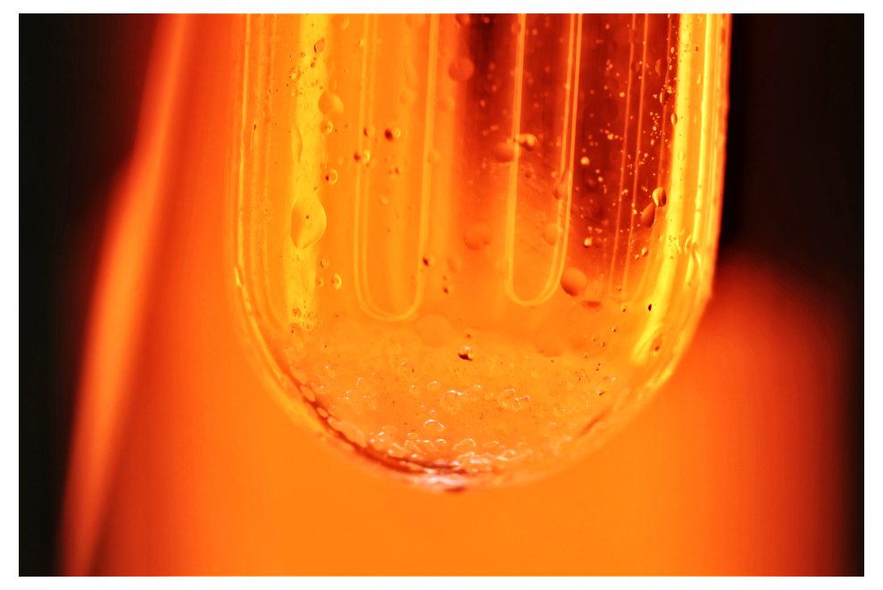
Experimental Parameters

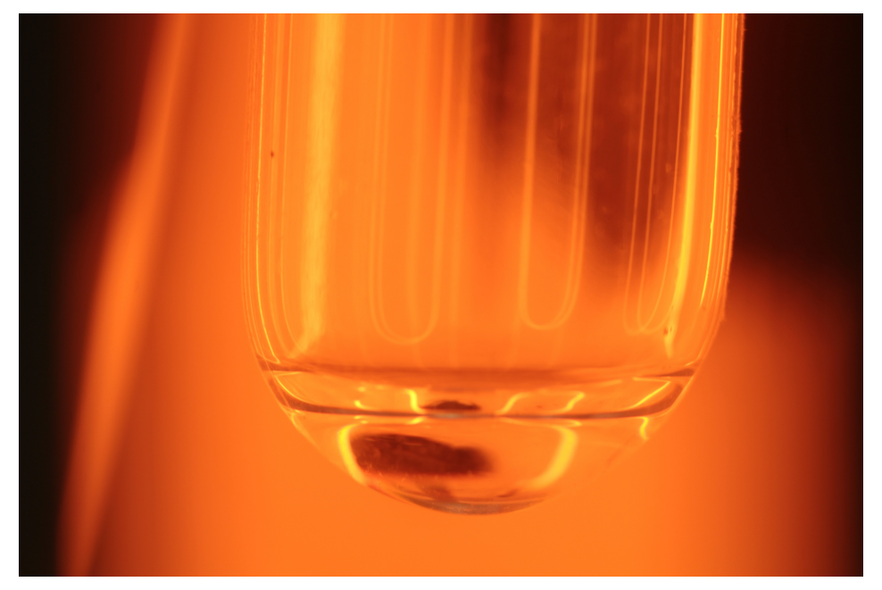
Residual Gas Analysis Mass Spectrometry

- Weigh one gram of sample in a quartz tube
- Suspend quartz tube in furnace
- Ramp at 10 °C/min to desired temperature and hold for 1.5 hours

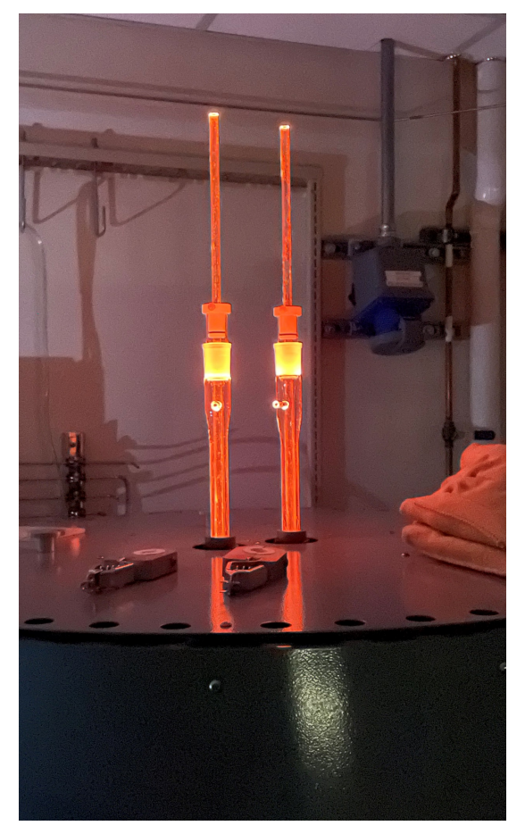
Preliminary Results







Heat Capacity & Enthalpy



Experimental Parameters

Differential Scanning Calorimetry

- Isothermal hold at 30 °C for 20 minutes to reach equilibrium
- Ramp rate 10°C/min to desired temperature and held for 20 minutes

Drop-Calorimeter

- 24 hour hold to fully equilibrize temperature
- Drop laser welded samples and wait for baseline to be met before next drop

Calculations

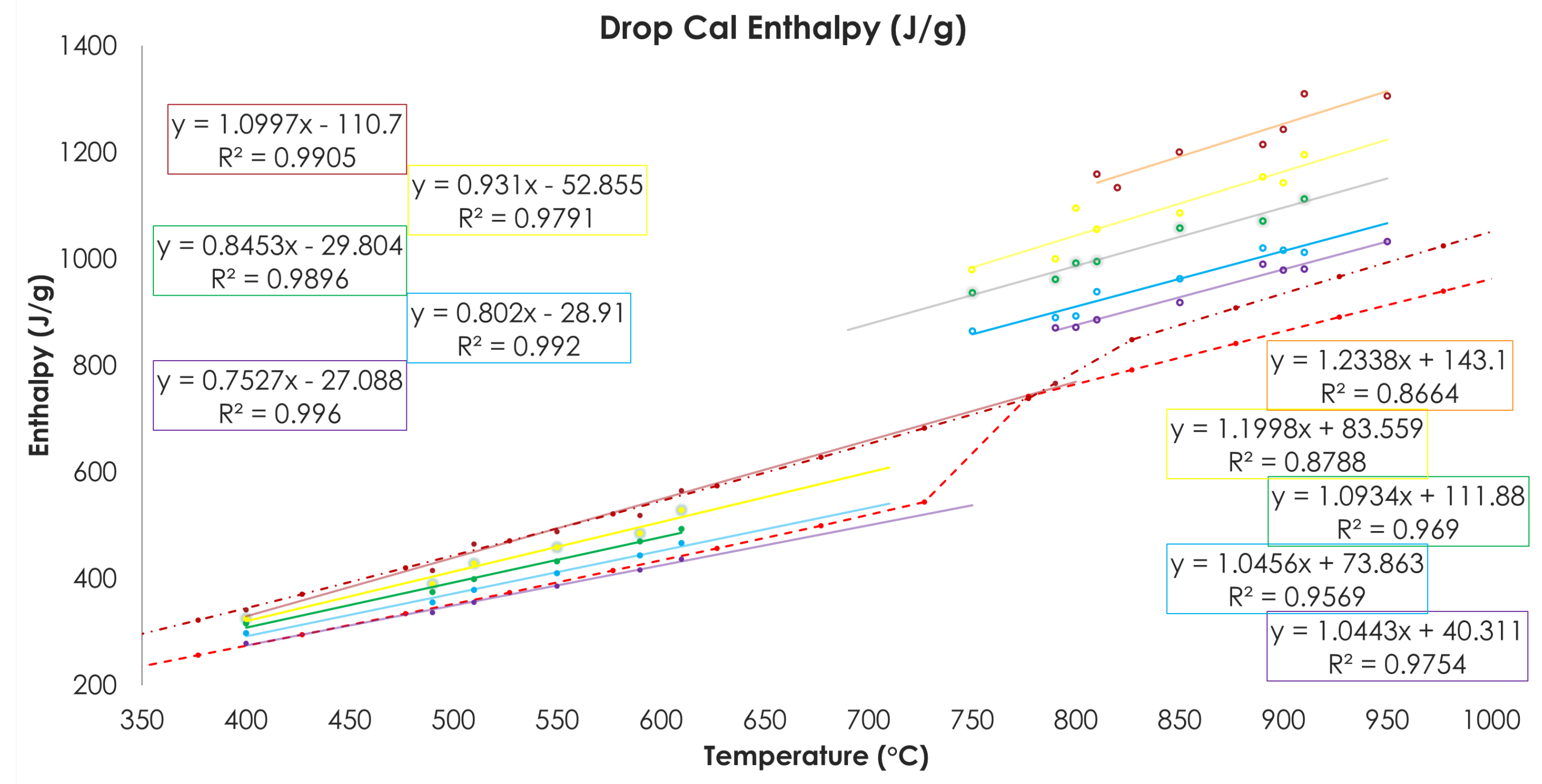
Step One:
$Q = C\Delta T$
$dH = \delta Q + Vdp$

Step Two (Constant Pressure):
$Vdp = 0$
$dH = \delta Q$

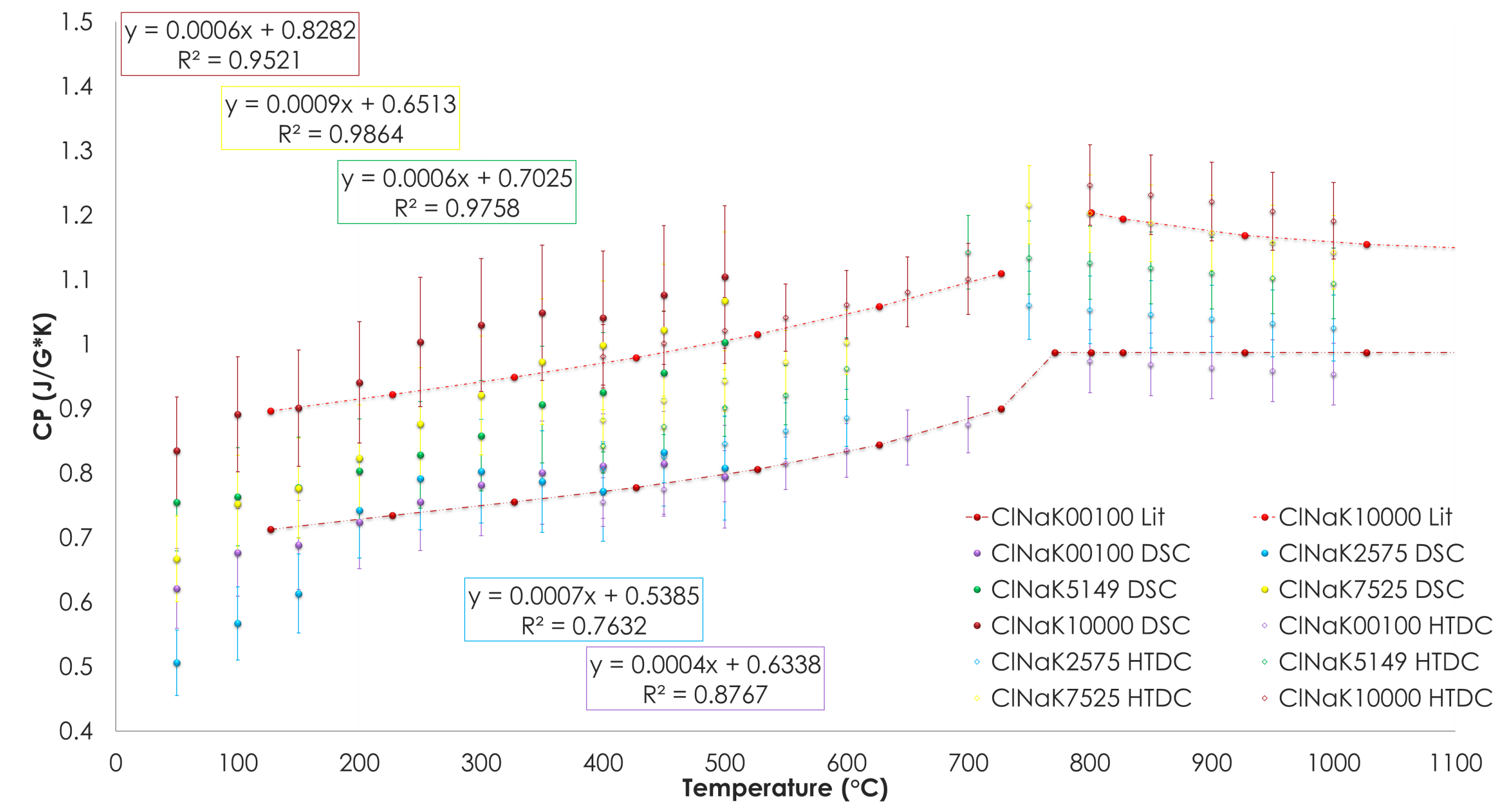
Step Three:
$C_p = (\delta Q / dT)$

Q = heat added
C = heat capacity
H = enthalpy
V = volume
T= Temperature

Results



Enthalpy determined with drop-calorimetry and compared to literature values



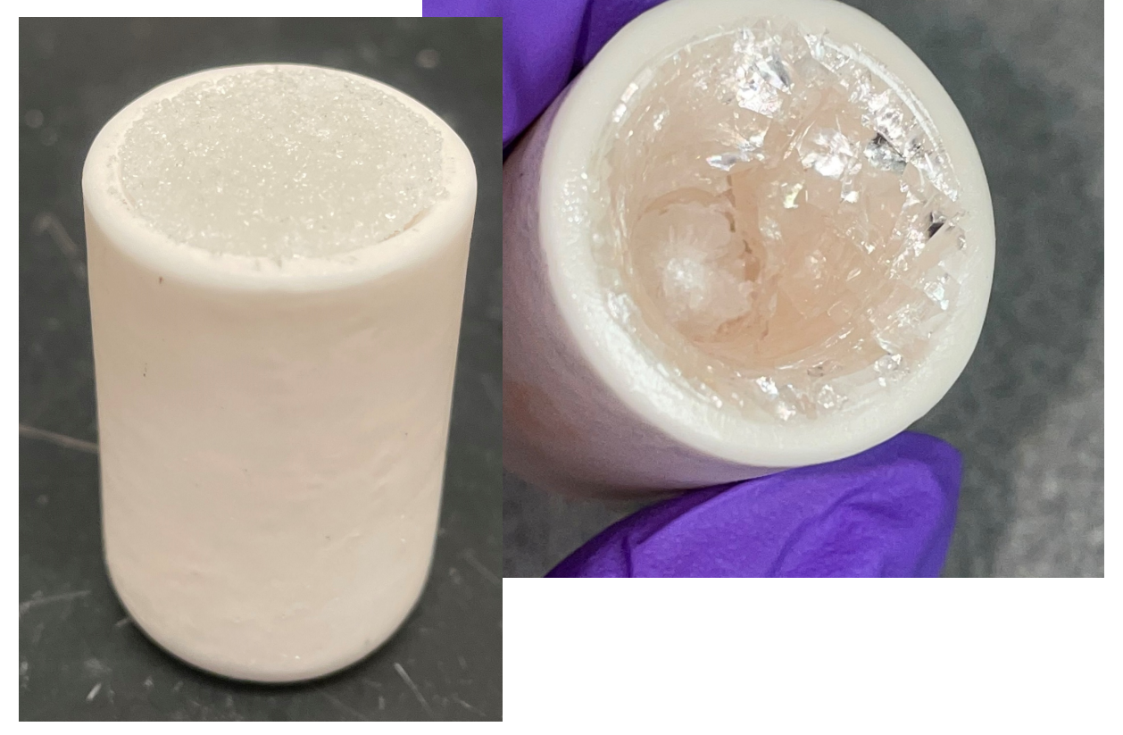
Heat capacity determined with drop-calorimetry and DSC and compared to literature values

Density Development

Experimental Parameters

- Weigh an alumina crucible and measure the dimensions with calibrated calipers
- Weigh out two grams of salt sample and add to crucible, record new total mass
- Place crucible into overflow crucible and into the furnace
  - Ramp rate of 10°C/min to 800°C
  - Held for 3 hours and ramped down to cooling at same rate
- Clean any overflow and take mass with and without residual

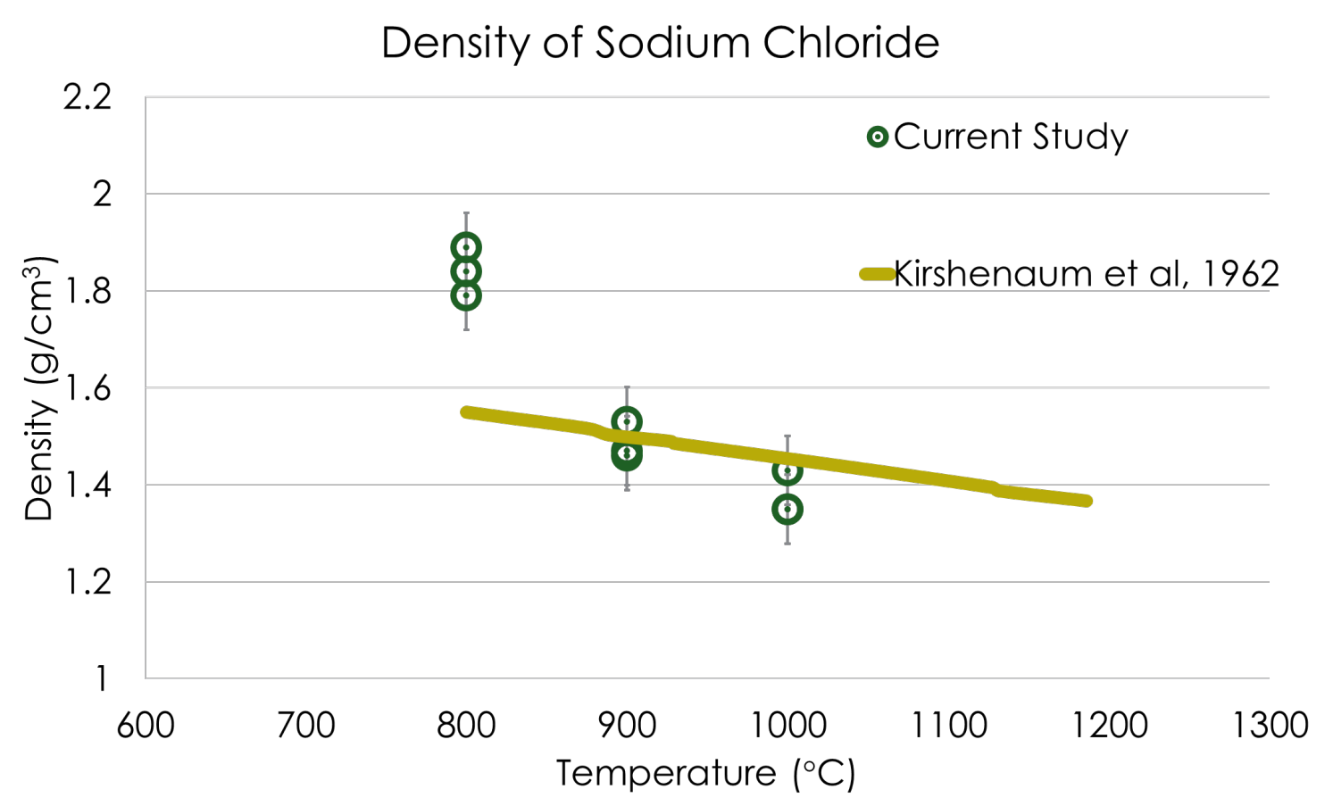
Calculations

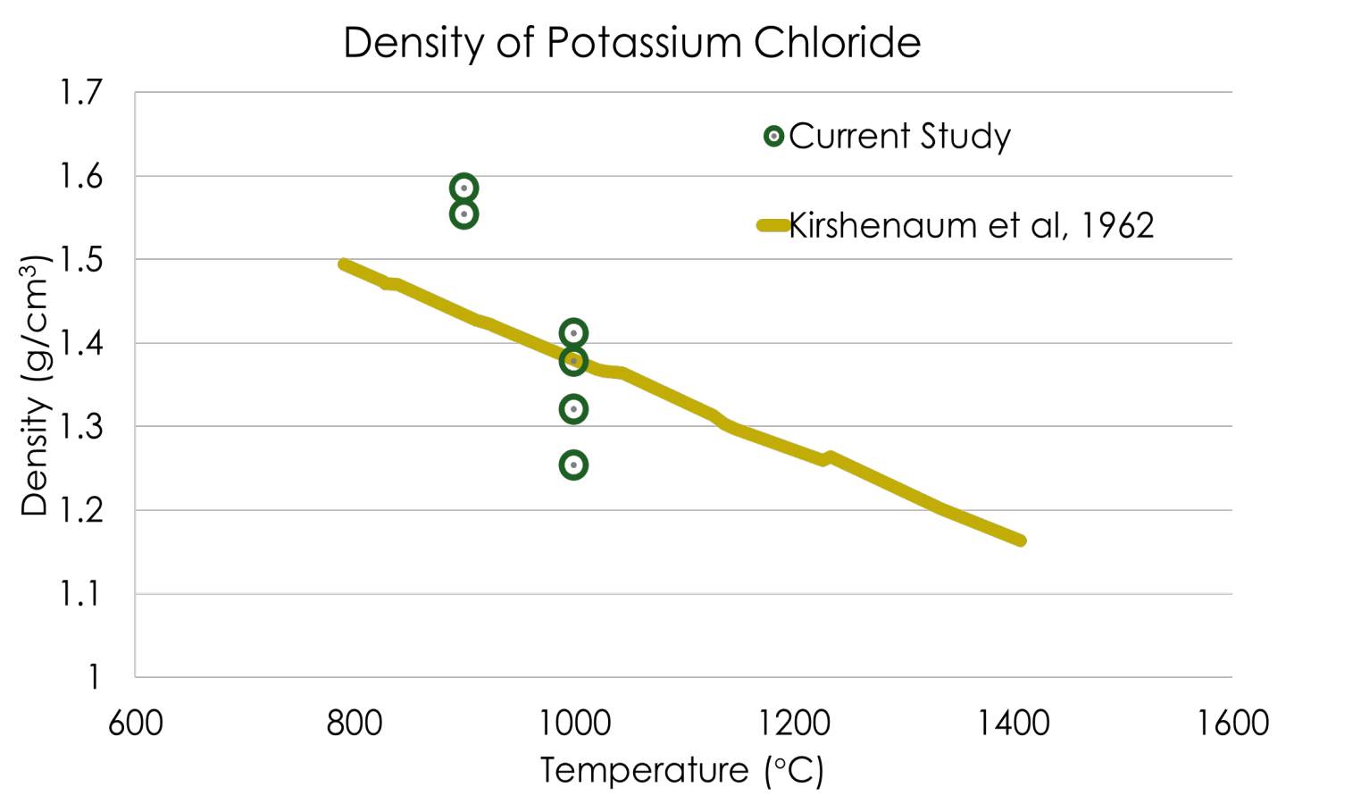


$$\rho = \frac{m_f}{V_i}$$

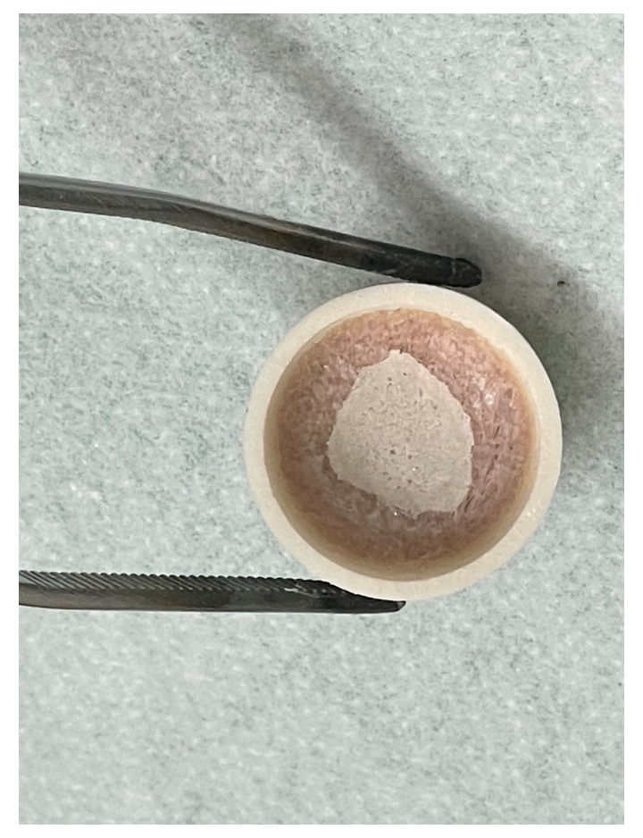
ρ = density
m_f = Final mass
V_i = Initial Volume

Results





Future Work



Continue development of vapor pressure and finish density studies with the benchmark sodium-potassium chloride system

Continue data collection of heat capacity and calorimetry with actinide bearing fuel salts

Adapt current methodology to safely handle and contain radiological material

Sources

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DOE MSR Campaign
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Evaluation of Nanomaterials in the Adsorption of Radioactivity for Continued Understanding of Nanodiamond Uses in Radiochemistry

By: Megan Zaiger, Dr. Ralf Sudowe*

Background

- Earthquake and tsunami caused accident at the Fukushima Nuclear Power Plant in 2011.
- Large amounts of radioactivity released into the ocean, soil and surface waters.
- After cleanup, large amounts of soil and water stored as waste.
- Radioisotope Cs-137 major concern due to long half-life of 30 years.
- Accurate measurement and recovery of Cs-137 necessary for remediation and waste disposal.

Objectives

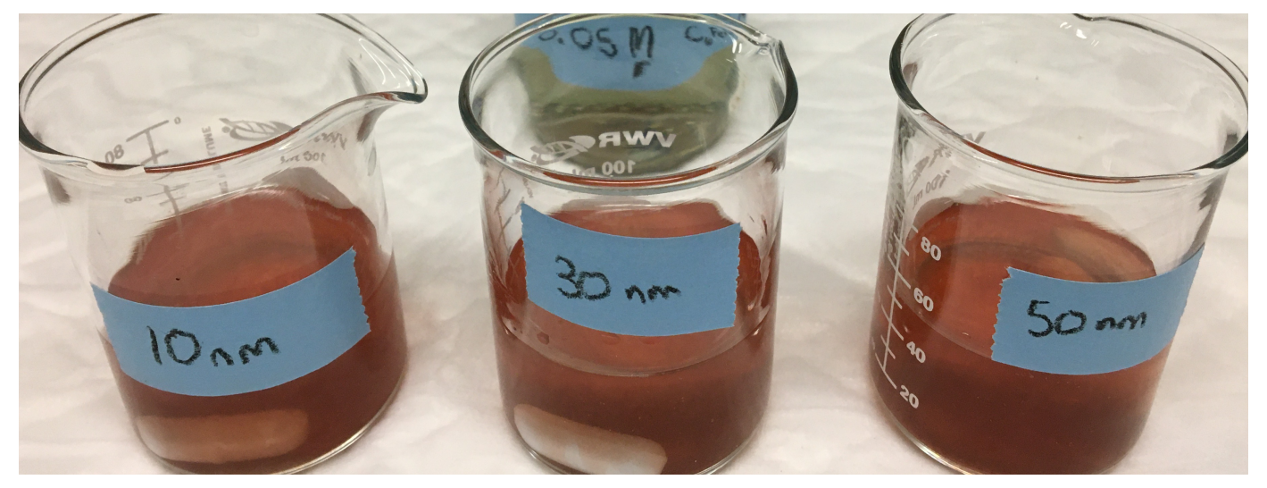
- Confirm results obtained for pure water.
- Utilize stable cesium carrier to improve recovery of radiocesium.
- Examine the influence of temperature and pH on uptake of radiocesium.
- Study the effect of interfering ions (Na, K, Mg) present in ocean water.
- Investigate adsorption rates in different media:
  - ➢ Simulated ocean and river water
  - ➢ Real ocean and river water

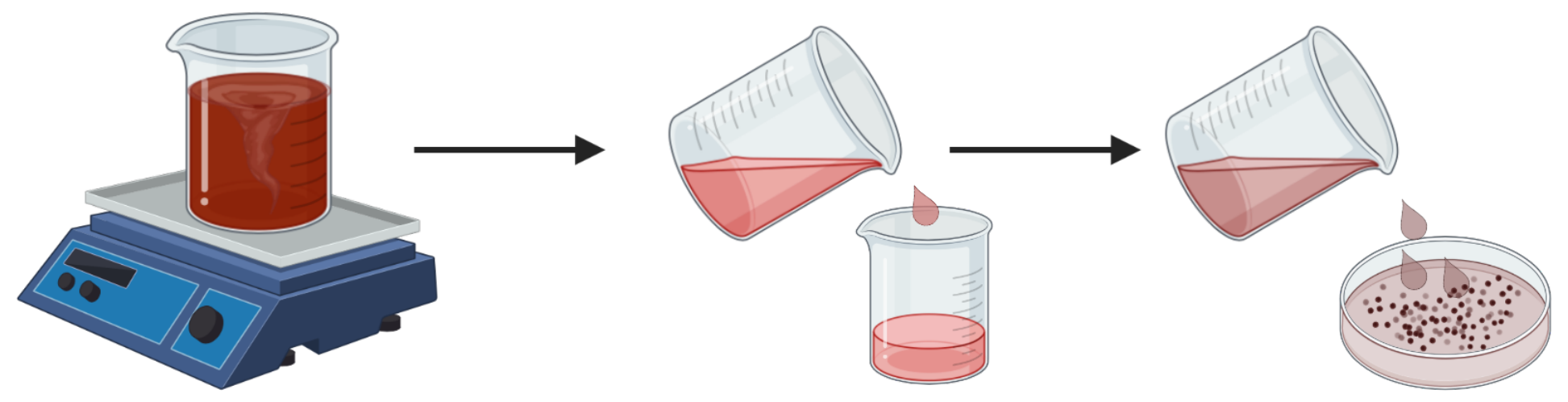
Methods

Pretreatment of Detonation Nanodiamonds

1. Dried ND solution in a crucible at 100°C.
2. Calcined DND in furnace at 400°C for 8 hours.
3. Diluted DND back to 1 % (w/w).

Adsorbent Preparation

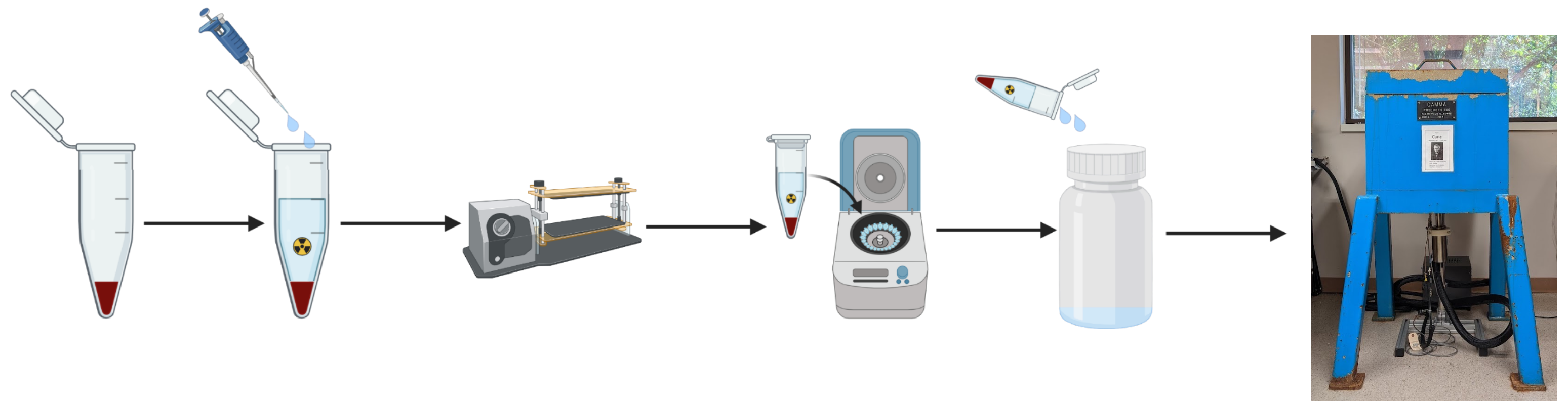




1:1:1 ratio of ND, 0.1 M CuCl2 , 0.05 M K4[Fe(CN)6]

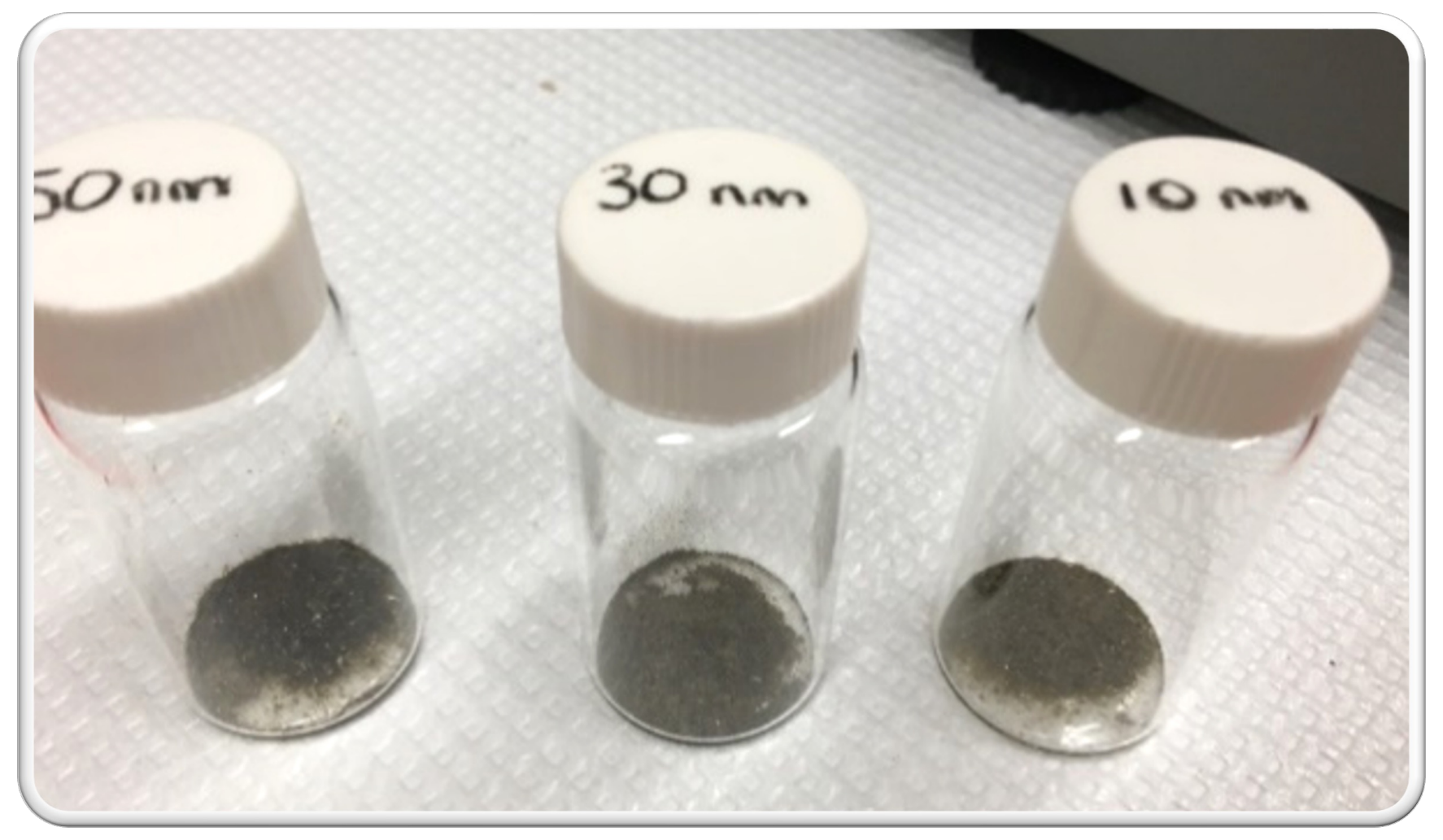
Pretreatment of Detonation Nanodiamonds

1. Massed amount of sorbent was added to a 15 mL centrifuge tube.
2. Deionized water and ^{137}Cs stock solution were added.
3. Sample was mixed for a fixed time.
4. Adsorbent was allowed to settle overnight and then centrifuged.
5. Supernatant was removed and counted for remaining Cs-137 activity.



Future Result Goals

- Determine the detection limits for radiocesium preconcentration from water samples.
- Analyze low-activity water samples taken in the vicinity of the Fukushima Daiichi Nuclear Power Plant.
- Utilize nanodiamonds to remove Cs-137 from waste water.
- Extend application of functionalized nanodiamonds to other radionuclides.



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Development of a Predictive Model to Quantify Exposure to Amorphous Silica Among Sugarcane Workers

Colton Castro.[1] Adgate, J.[2] Butler-Dawson, J.[2] Erlandson, G.[1] Seidel, J.[1] Calvimontes-Barrientos, L.[1] Newman, L.[2] Schaeffer, J.[1]

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Introduction

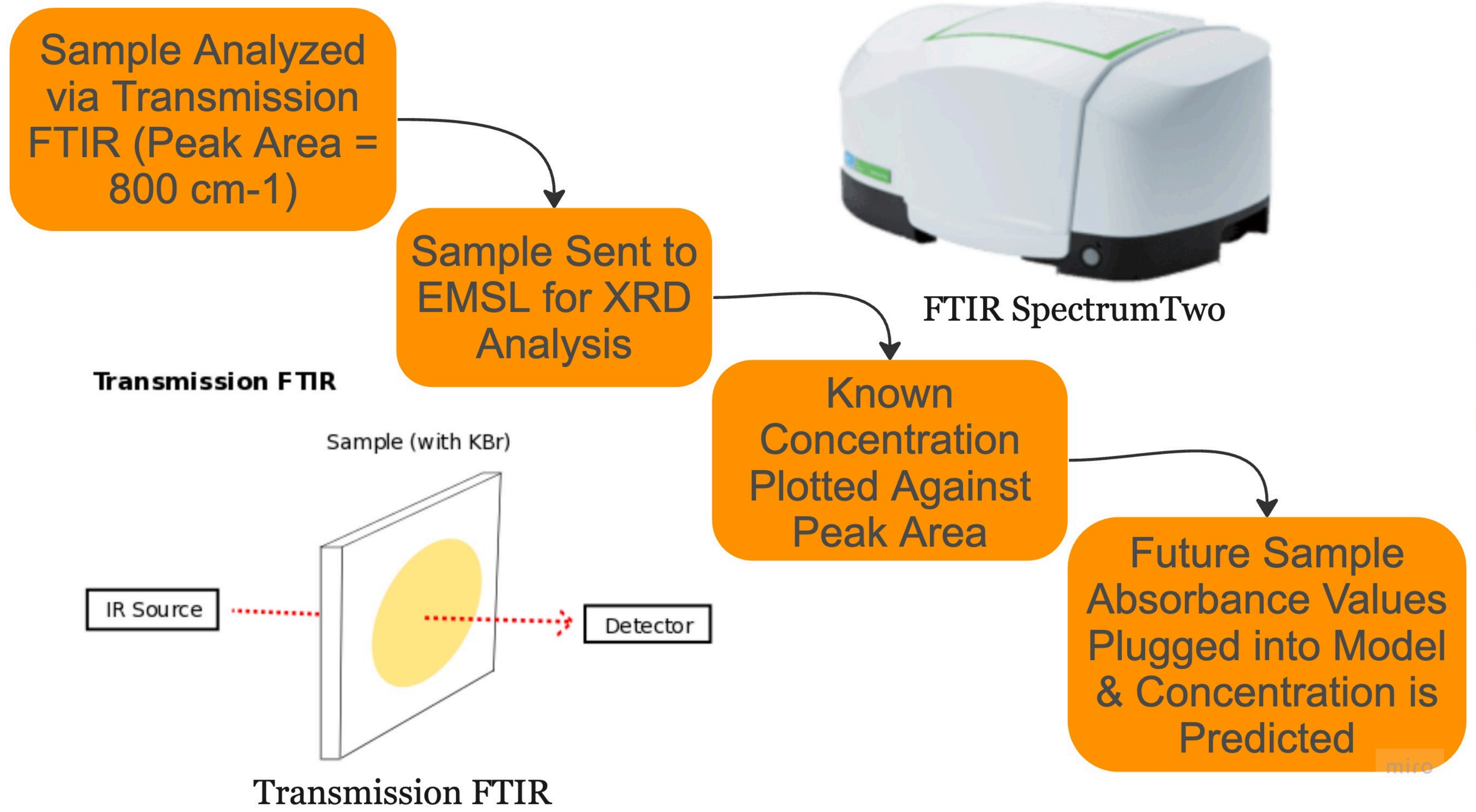
Background: Sugarcane harvesters in Central America continue to experience a heavy burden of chronic disease of unknown etiology (CKDu). These workers are exposed to high concentrations of particulate matter comprised of nephrotoxicants – e.g., silica. The health impacts of amorphous silica remain largely understudied, especially in conjunction with other risk factors (thermal stress and dehydration). Exposure assessments for amorphous silica are challenging due to:

- the non-crystalline structure, destructive analytical methods (e.g., NMAM 7501), and high costs of analysis

Aim: Develop a low-cost, non-destructive method to rapidly quantify amorphous silica.

Hypothesis: Fourier-Transformed-Infrared-Spectroscopy (FTIR) is a non-destructive method used by NIOSH to quantify crystalline silica. We hypothesize that a similar method and predictive model can be developed to measure amorphous silica in personal air samples.

Methods



Sample Analyzed via Transmission FTIR (Peak Area = 800 cm-1)

Sample Sent to EMSL for XRD Analysis

Known Concentration Plotted Against Peak Area

Future Sample Absorbance Values Plugged into Model & Concentration is Predicted

Figure 1: Diagram of proposed method

Results

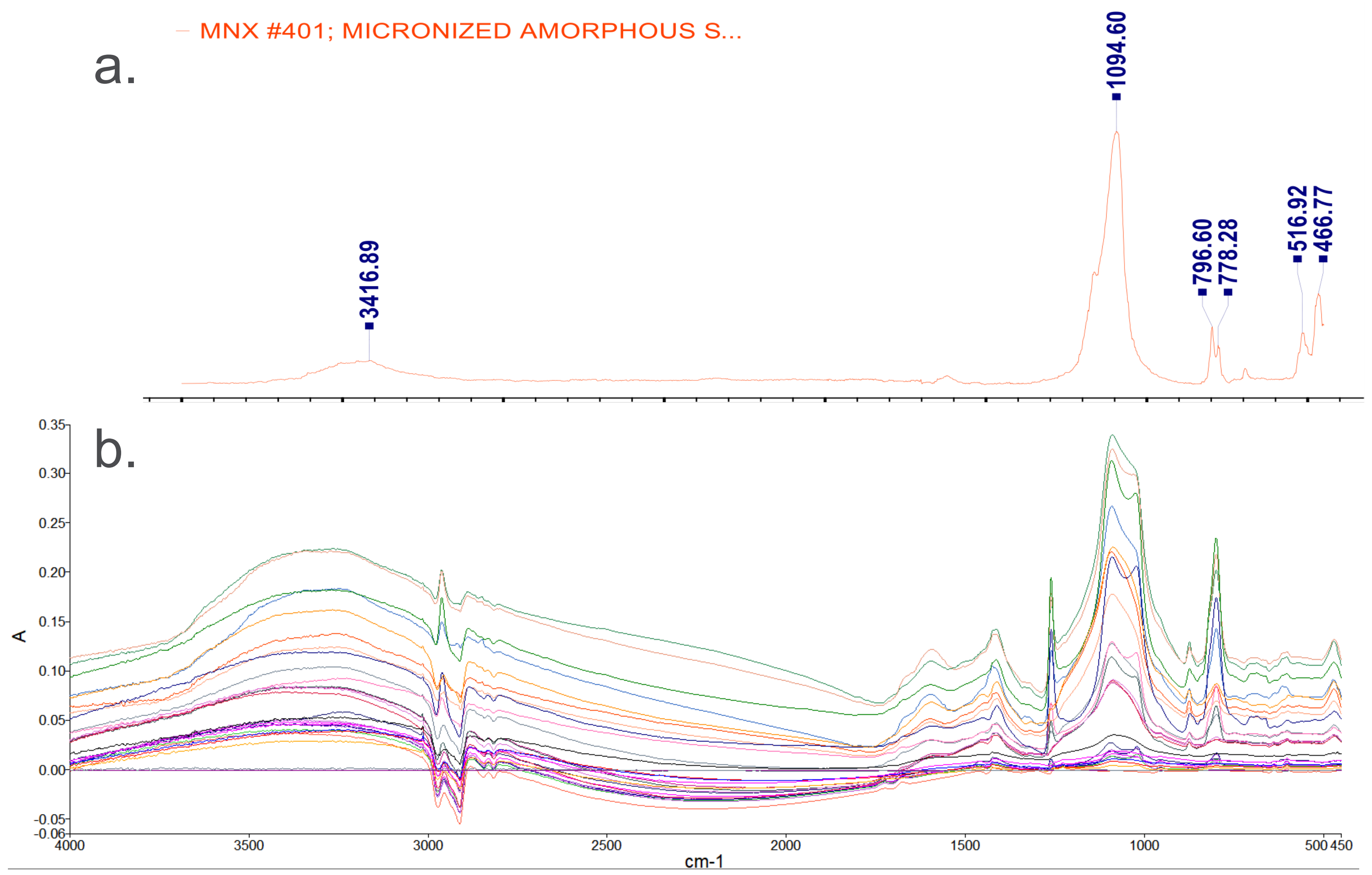


Figure 2: (a) Spectra of micronized amorphous silica from database, (b) Infrared spectra acquired from air samples (n=28)

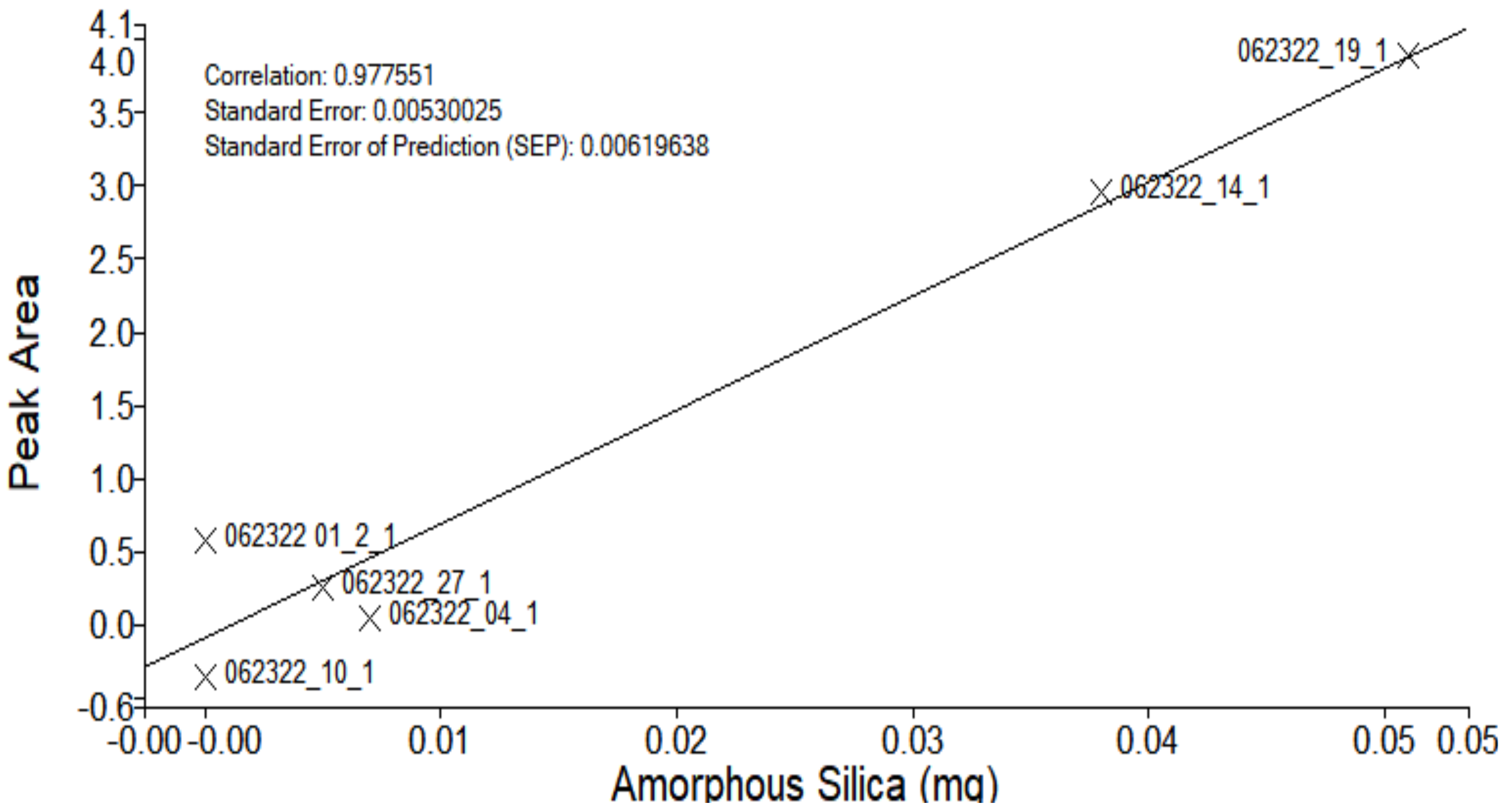


Figure 3: Predictive model relating concentration & peak area

Discussion

Several key features can be interpreted:

- We observed similarity between air samples and laboratory analyzed amorphous silica IR readings (Figure 2a and Figure 2b):
    - XRD-determined no crystalline silica in air samples
    - XRD-determined amorphous silica values of 0.007 – 0.05 mg in air samples
- We see that 800 cm^{-1} is an accurate peak to use for amorphous silica analysis (Figure 3):

Limitations of this project include:

- Low sample size of XRD-calculated concentrations of amorphous silica
- Samples with variability between current XRD-calculated values

Conclusions

This study is one of the first attempts to quantitate amorphous silica using an alternative method to NIOSH NMAM 7501. NIOSH developed an alternative method to NMAM 7500 for a coal-mine setting using FTIR, owing to the portability, and ability to acquire an IR spectra in a matter of seconds. A major advantage of this technique is the non-destructive nature, preserving the sample, allowing for other analyses to be conducted on the filter. This model supports current literature that amorphous silica is present as a particulate in sugarcane workers daily activity. Recent literature demonstrated a potential mechanism for amorphous silica nanoparticles to damage the kidneys in rat models, but future research is needed. Future directions will include adding samples to the model and investigating more advanced chemometric models that can detect smaller differences.

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Evaluating Noise Exposure in a Manufacturing Setting

By Darren Gieseck

Background

Manufacturing settings can often be loud and uncomfortable for employees. Especially metal working facilities. Previous studies have found that employees working in these types of environments can be at a greater risk for permanent hearing loss.

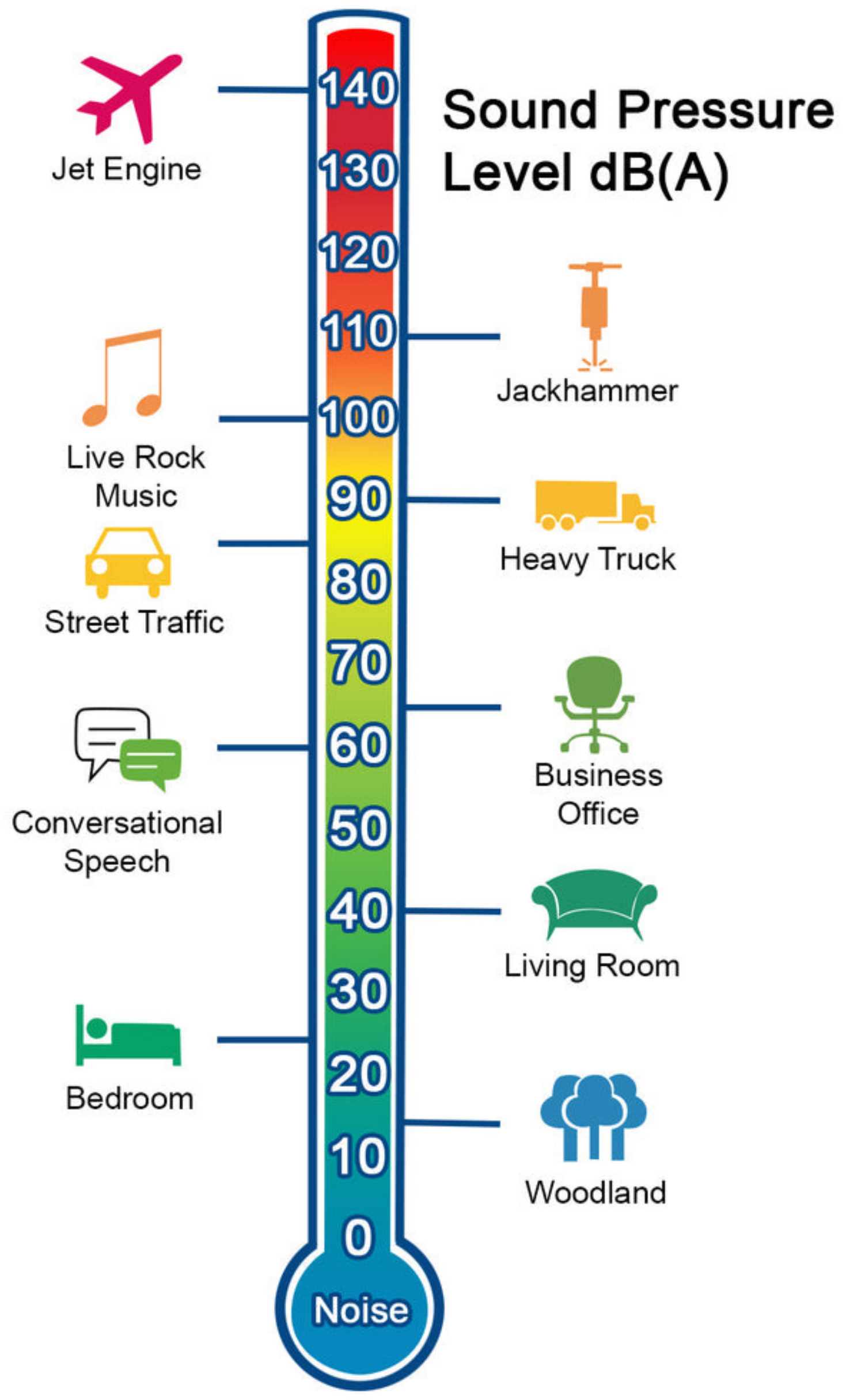
Objectives

- 1/3 octave band analysis and equipment assessment.
- Creation of a noise map of the facility which outlines the areas of greatest concern.
- Obtain individual noise sampling data to assess exposure for production line employees.
- Determine if employees in a specific metal manufacturing setting are overexposed to noise.
- Provide recommendations for sound mitigating materials.

Methods

- A sound level meter will be used to complete a 1/3 octave band analysis for noise map creation/equipment characterization.
- Personal noise dosimeters will be used to determine individual exposure.

https://www.tekcoplus.com/products/tk269plus



https://calright.com/product/extech-sl400-personal-noise-dosimeter/

Expected Results

- Noise map shows the areas of greatest concern within the facility.
- 1/3 octave band analysis highlights equipment of concern.
- Production line employees within these areas of concern are exposed to a noise level of 85dB or greater.
- Recommendations for sound mitigation are provided to the facility for future noise control.

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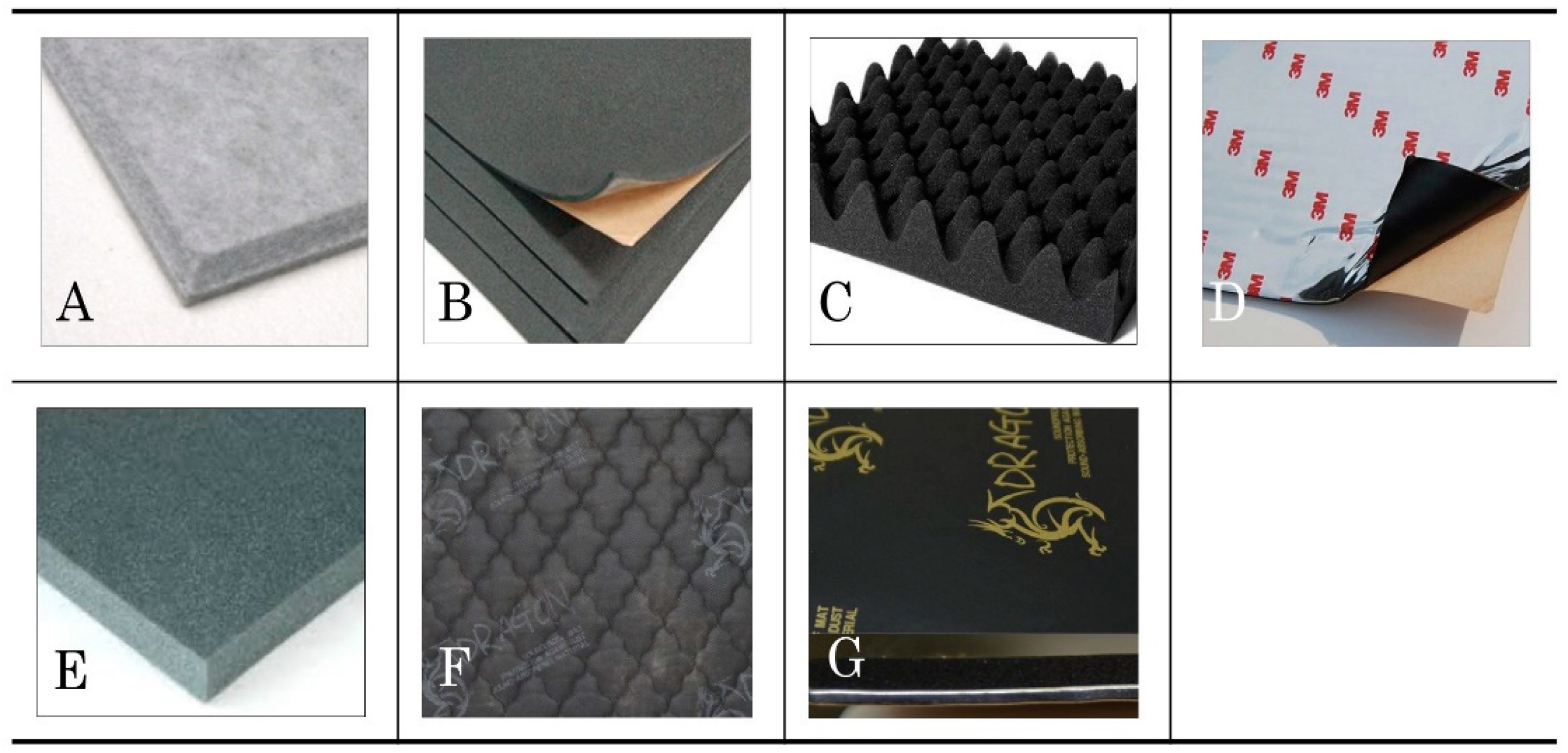


https://www.mdpi.com/2076-3417/10/8/2768

Community Noise Exposure from Nearby Oil and Gas Extraction Sites

Phillip Stepherson - Colorado State University

Introduction

As the Colorado oil and gas (O&G) industry expands, its extraction and production activities are encroaching on residential areas, which may increase the risk of harmful noise exposure to community residents.

- Colorado is the 4th largest oil-producing state in the United States with more than 122,000 total wells including more than 37,000 active-producing wells.
- 502 new drilling permits were issued during 2022, a 178% increase from 2021.
- The Colorado Oil and Gas Conservation Commission (COGCC) has identified multiple sources of high-volume sound associated with oil and gas site preparation, drilling and fracking

Objectives

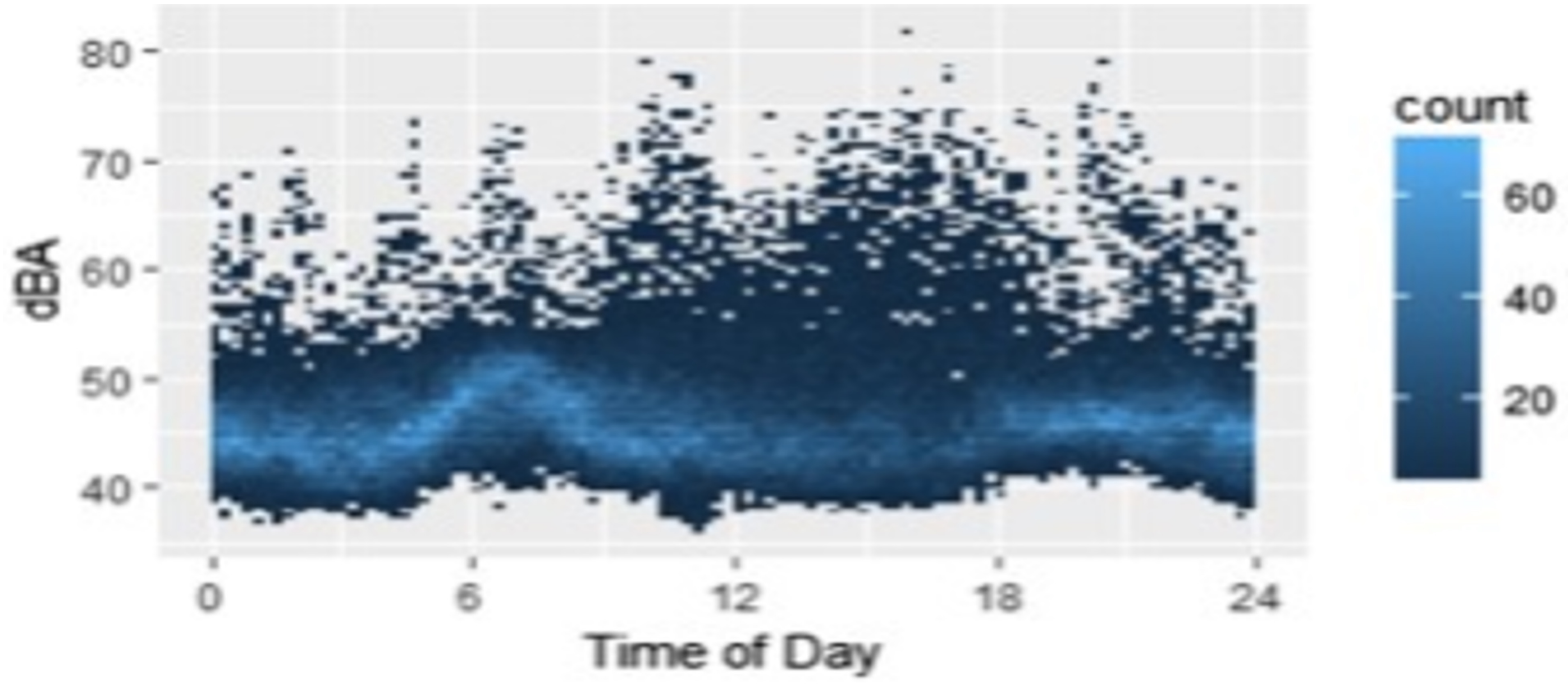
The purpose of this study is to compare noise survey data to COGCC limits to determine if community members overexposed to O&G related noise. The results from the data analysis will be used to answer the following questions:

- Are O&G companies exceeding COGCC noise limits?
- Are community members at risk of adverse health effects due to noise exposure from O&G operations?
- Do noise exposure levels vary significantly between different phases of O&G operations?

Methods

Measurements

Description	Time Period	Units
Leq: average sound pressure level (SPL) over monitoring period	24hr	dBA
Leq-Day (7 AM to 7 PM)	12hr	dBA
Leq-Night (7 PM to 7 AM)	12hr	dBA
Noise level exceed 10% of the time	24hr	dBA
Community Noise Equivalent Level	24hr	dBA
Exceedance Fraction: 65 dBA Day	12hr	%
Exceedance Fraction: 60 dBA Night	12hr	%
Exceedance Fraction: 65 dBC Day	12hr	%
Exceedance Fraction: 65 dBC Night	12hr	%



Example of O&G noise data

Monitoring Equipment

Larson Davis NMS044 Portable Noise Monitoring System

Extraction Phases

- Site Preparation
- Drilling
- Hydraulic Fracturing
- Flowback

Noise Survey

- Data will be collected at three different well-pads.
- The system will be placed at 350' from the well pad for "close" monitoring and at 1,975' for "far" monitoring with sampling periods of either 12 hours or 24 hours.
- Data will be downloaded and analyzed using the Larson Davis G4 LD Utility Software.
- Noise levels will be analyzed respectively for each phase of extraction

Expected Results

There is currently very limited data on community noise exposure from O&G extraction operations. Literature suggests a higher risk of exposure to low-frequency sound. The primary health effects from oil and gas extraction noise exposure are:

- Annoyance
  - increased feelings of anger, anxiety, helplessness and exhaustion
- Sleep disturbance
  - insomnia, sleep interruption, and increased drug use
- Adverse cardiovascular effects
  - elevated blood pressure, hypertension, ischaemic heart disease, and stroke

What have studies shown?

- An average of 65 dbA and 79dBC during drilling at a distance of 350'
- An average of 69.5dBA and 80dBC during fracking at a distance of 350'
- Noise levels as high as 73 dBA during all phases of extraction at a distance of 625'

These data suggests that O&G extraction sites are likely violating COGCC noise limits and is strong preliminary evidence to suggest that community members are at an increased risk of adverse health outcomes.