LA-UR-17-30100

Title: Non-Invasive Acoustic-Based Monitoring of Heavy Water and Uranium Process Solutions

Author(s): Pantea, Cristian
Sinha, Dipen N.
Lakis, Rollin Evan
Beedle, Christopher Craig
Davis, Eric Sean

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Non-Invasive Acoustic-Based Monitoring of Heavy Water and Uranium Process Solutions

Cristian Pantea, Dipen Sinha, Rollin Lakis, Chris Beedle, Eric Davis

Oct 26, 2017

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Agenda

- Introduction
- Heavy Water Challenge
- Swept-Frequency Acoustic Interferometry
- Results for Heavy Water Experiments
- Uranium Process Solution Challenge
- Results for Uranium and Nitric Acid Solutions
- Summary

Project Goals

- Leverage Laboratory scientific strength in physical acoustics for critical international safeguards applications
- Create hardware demonstration capability for noninvasive, near real time, and low cost process monitor to capture future technology development programs
- Measure physical property data to support method applicability

Heavy Water Production Monitoring: A New Challenge for the IAEA

Arak Heavy Water Production Facility
Girdler sulfide process + distillation

JCPOA-130 metric ton limit

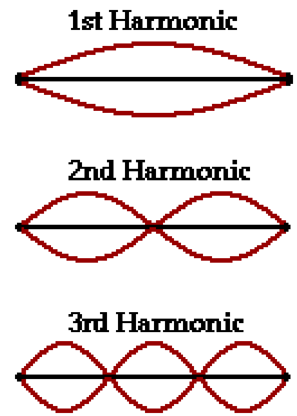
Swept-Frequency Acoustic Interferometry

SFAI (Swept-Frequency Acoustic Interferometry) is based on setting up Standing Waves and Resonances in a Fluid medium inside a cavity:

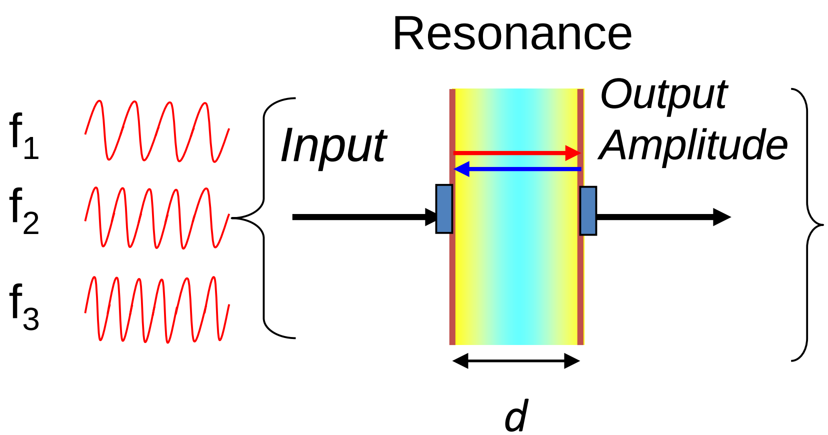
Resonance occurs when:

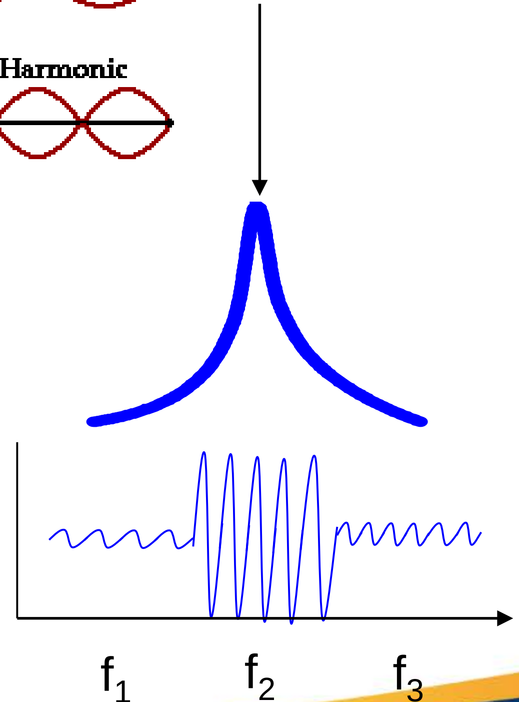
$$d = n.(\lambda/2)$$

n=1, 2, 3…
λ=wavelength



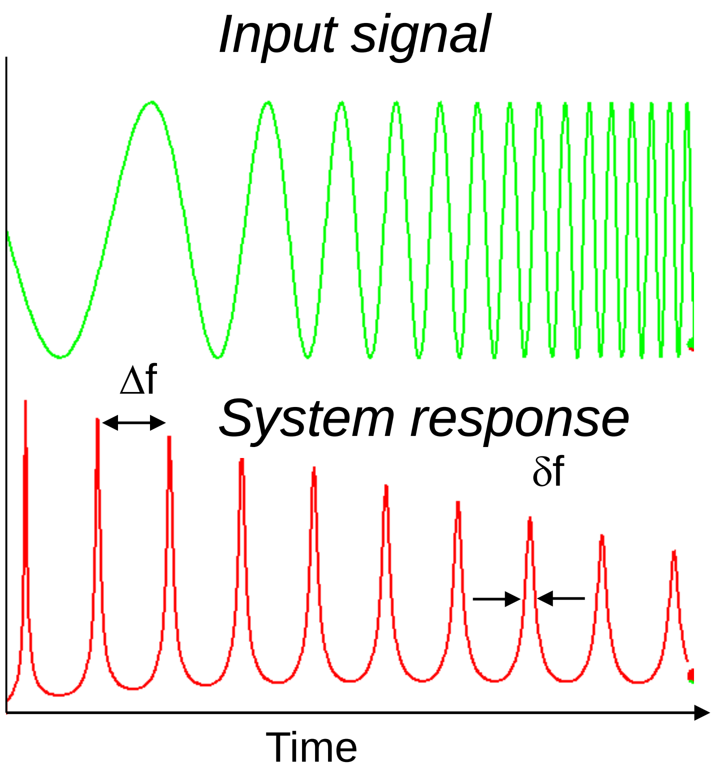
Examples of standing wave when resonance occurs





Swept-Frequency Acoustic Interferometry

How are fluid properties determined using swept frequency and acoustic interferences?



Sound speed = $2d\Delta f$

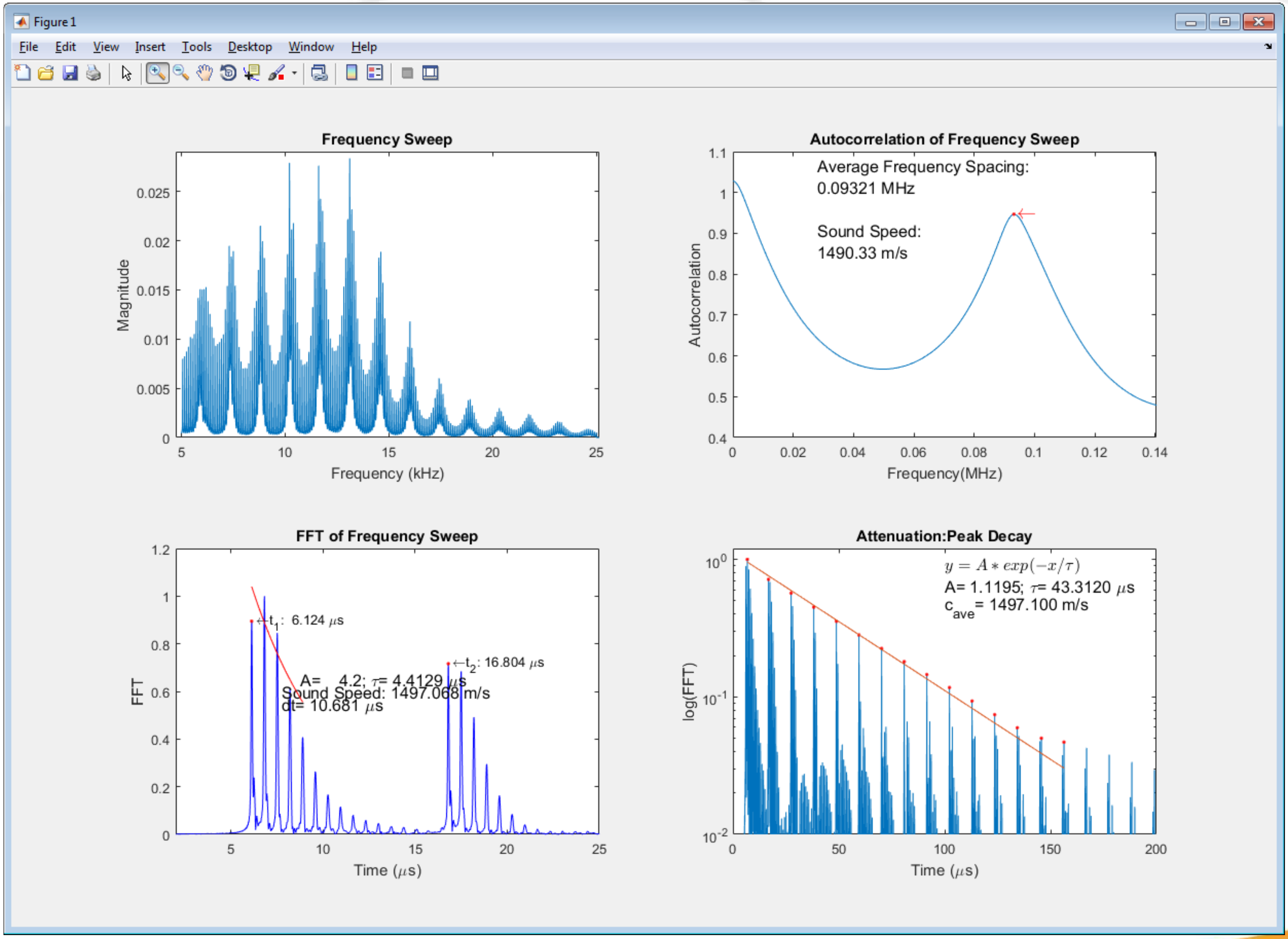
Sound absorption ✪ δf

Δf =frequency spacing

δf =peak width

There can be hundreds of such resonance peaks in a typical spectrum

Developed GUI (Matlab)



Large Scatter in Literature Values

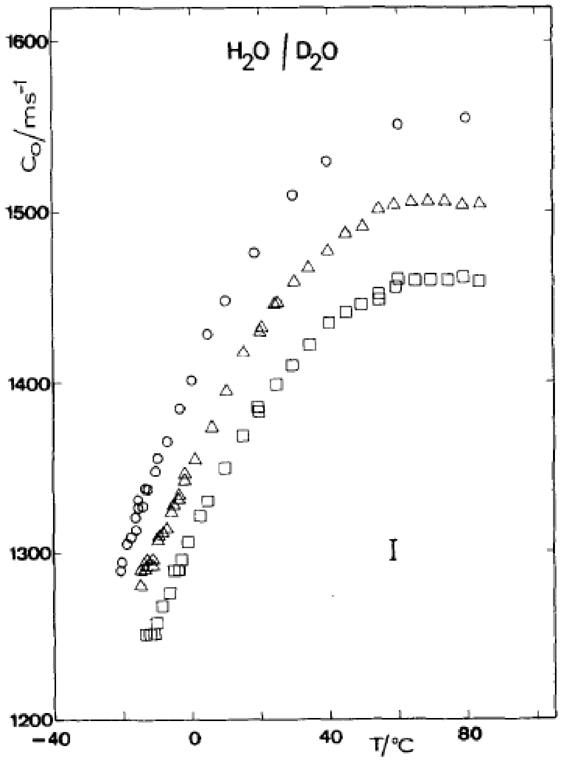
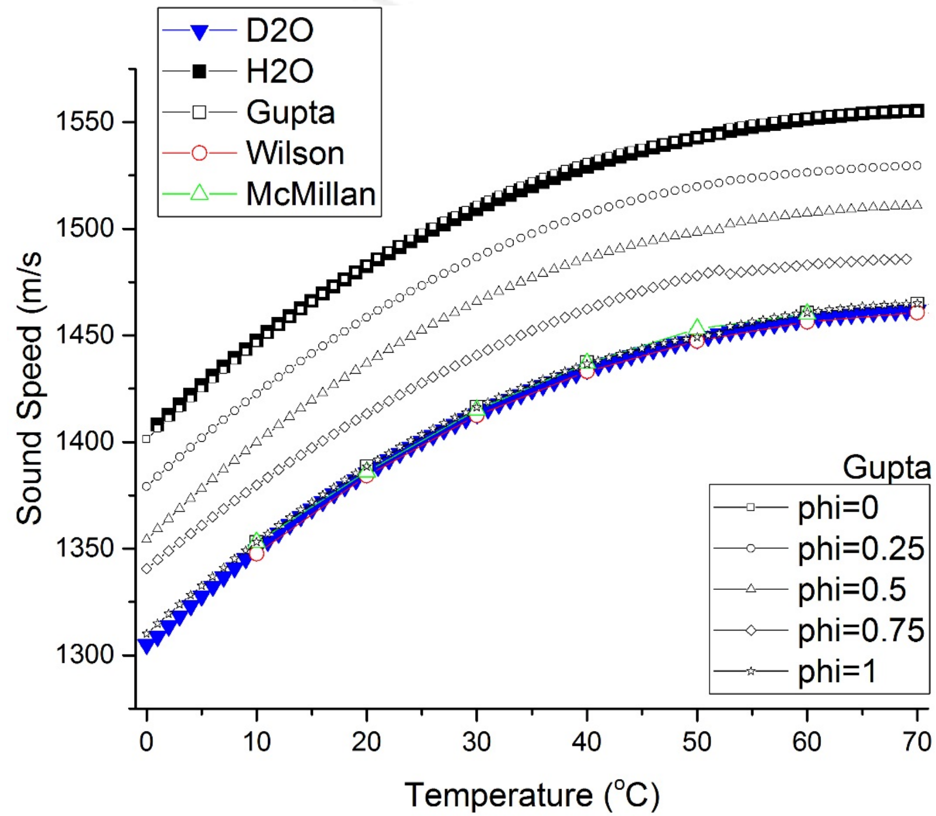


FIG. 1. Sound velocity vs temperature in ○: pure H_2O; □: pure D_2O; Δ: $(H_2O)_{0.525}(D_2O)_{0.475}$ solution.

Conde, J. Chem. Phys. 76(7), 1 Apr. 1982

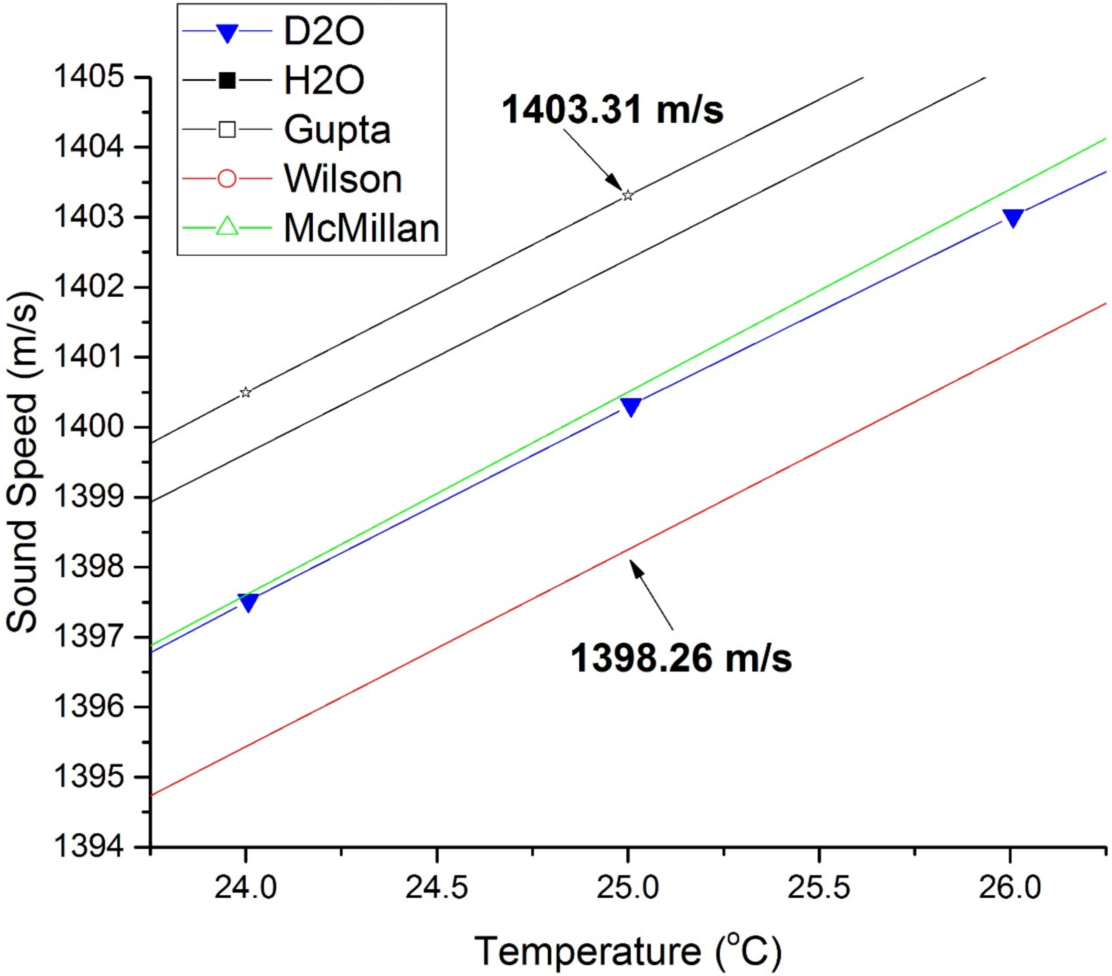


Gupta, J. Chem. Thermodynamics 1976, 8,627
Wilson, JASA 1961, vol 33, no. 3, 314
McMillan, JASA 1947, vol 19, no. 6, 956

Literature: old data
Large scatter

D_2O purity not well known

Large Scatter in Literature Values



Literature data at 25°C for **'pure' D_2O** show a scatter of about **5%** in concentration.

*Wilson used 99.82% D_2O

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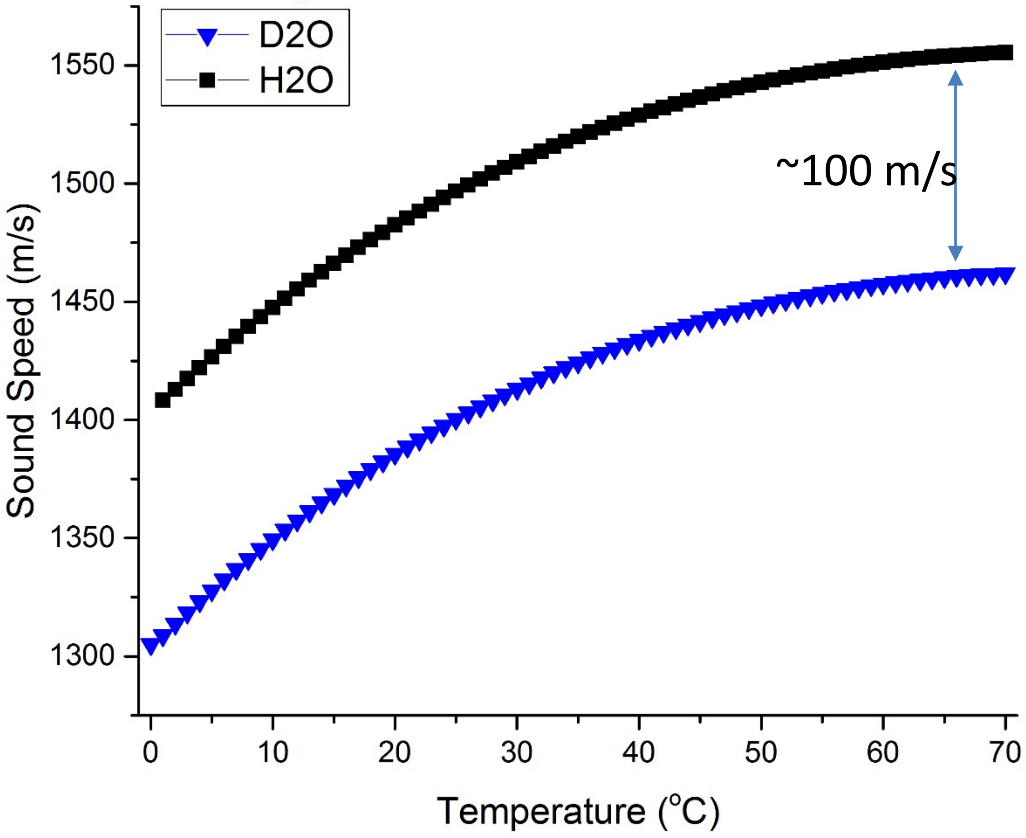
Highest Precision Sound Speed Data Available: New Standard in H/D



!Reference data – calibration curve

We can measure accurate and precise sound speed, to the first decimal point

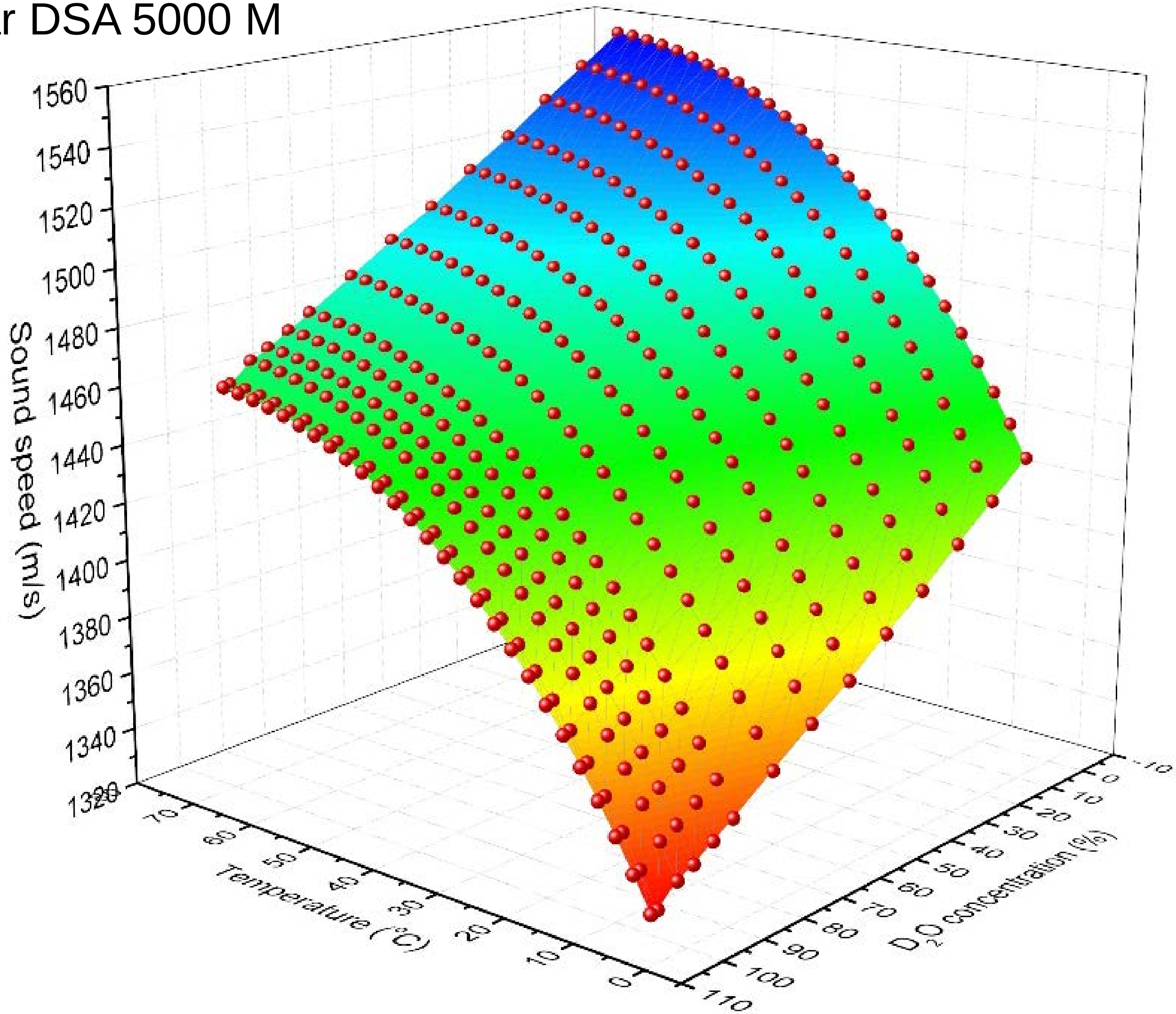
→ high precision/accuracy for D_2O concentration, ~ 0.1%

nuclear reactor grade:
99.75–99.98% deuterium enrichment

*precisions of ± 0.2-0.4% using other methods, gravimetric, float bath, displacement, mass spectrometry, IR Spectroscopy, emission spectroscopy, nuclear magnetic resonance, cryoscopy, refractometry, etc.)

~400 pts of data

Calibration data taken with a Density and Sound Velocity Meter: Anton-Paar DSA 5000 M



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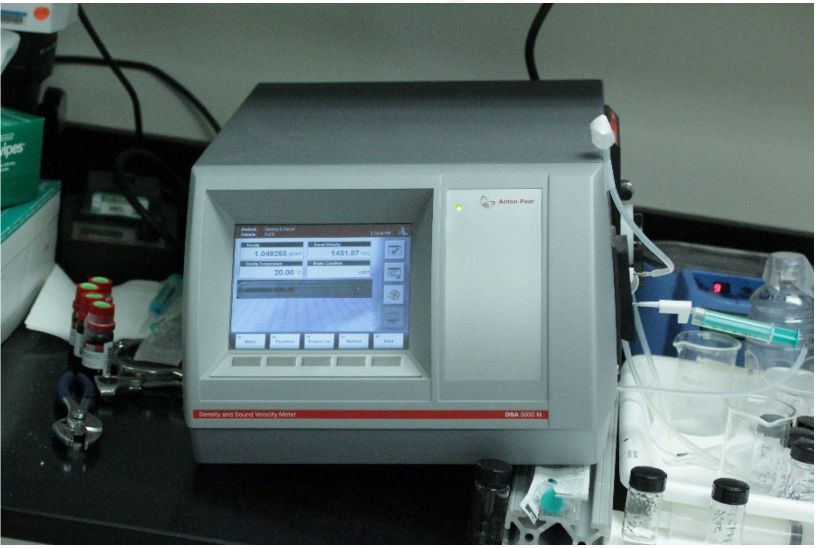
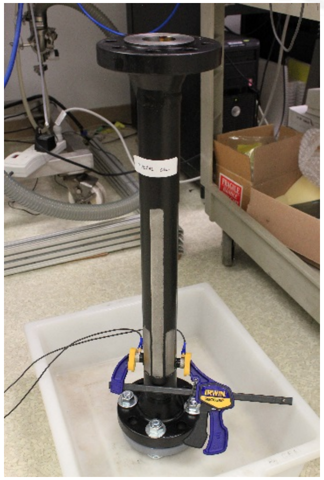
Noninvasive Measurements in SFAI Cell

Lab environment

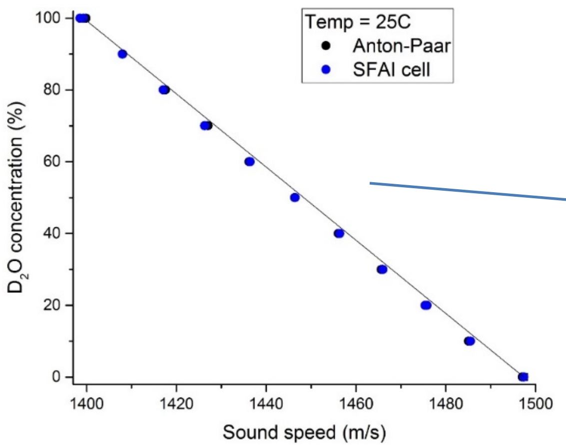


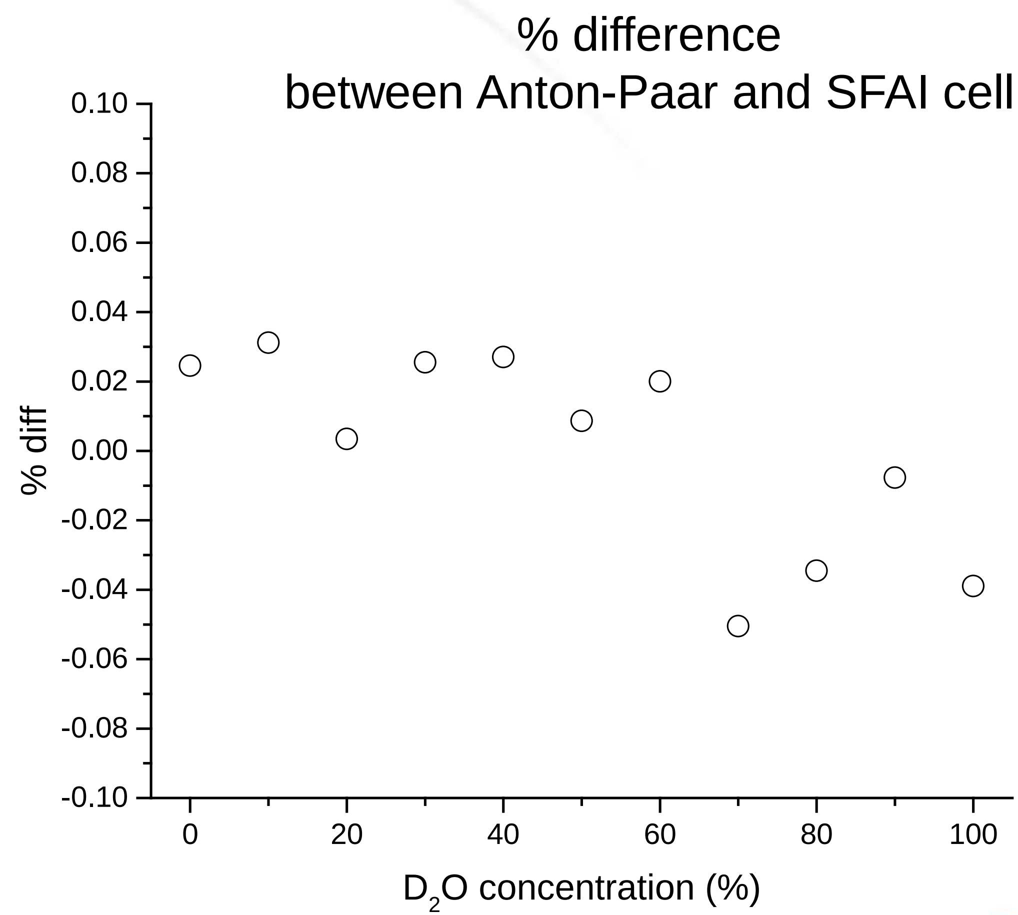
Anton-Paar

Field



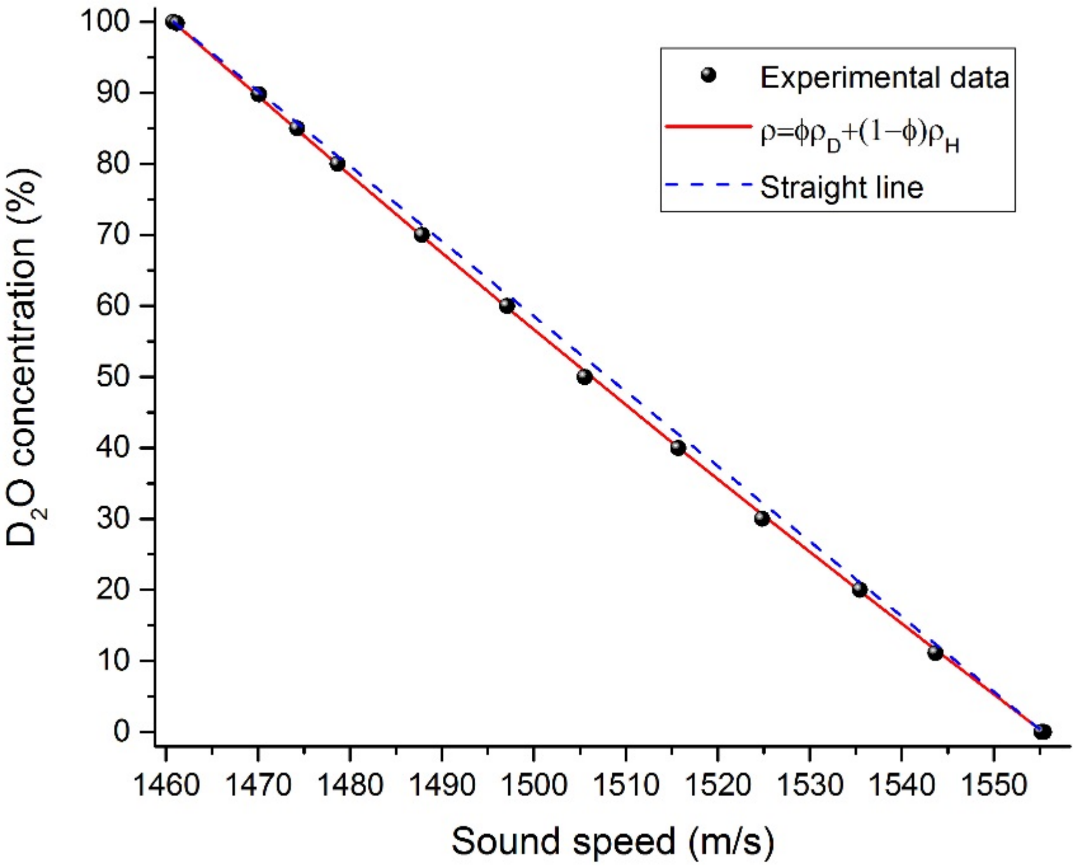
Noninvasive Measurements in SFAI Cell





Simple Binary Mixing Rule

Mixture law: Urick model



Simple linear combination based on the volume fraction φ:

$\rho=\varphi\rho_D+(1-\varphi)\rho_H$,

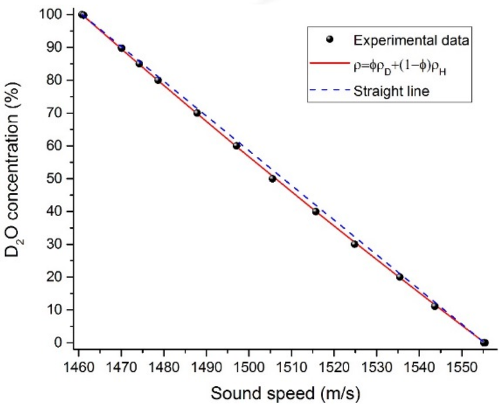
ρ_D - density of pure D_2O

ρ_H - density of pure H_2O

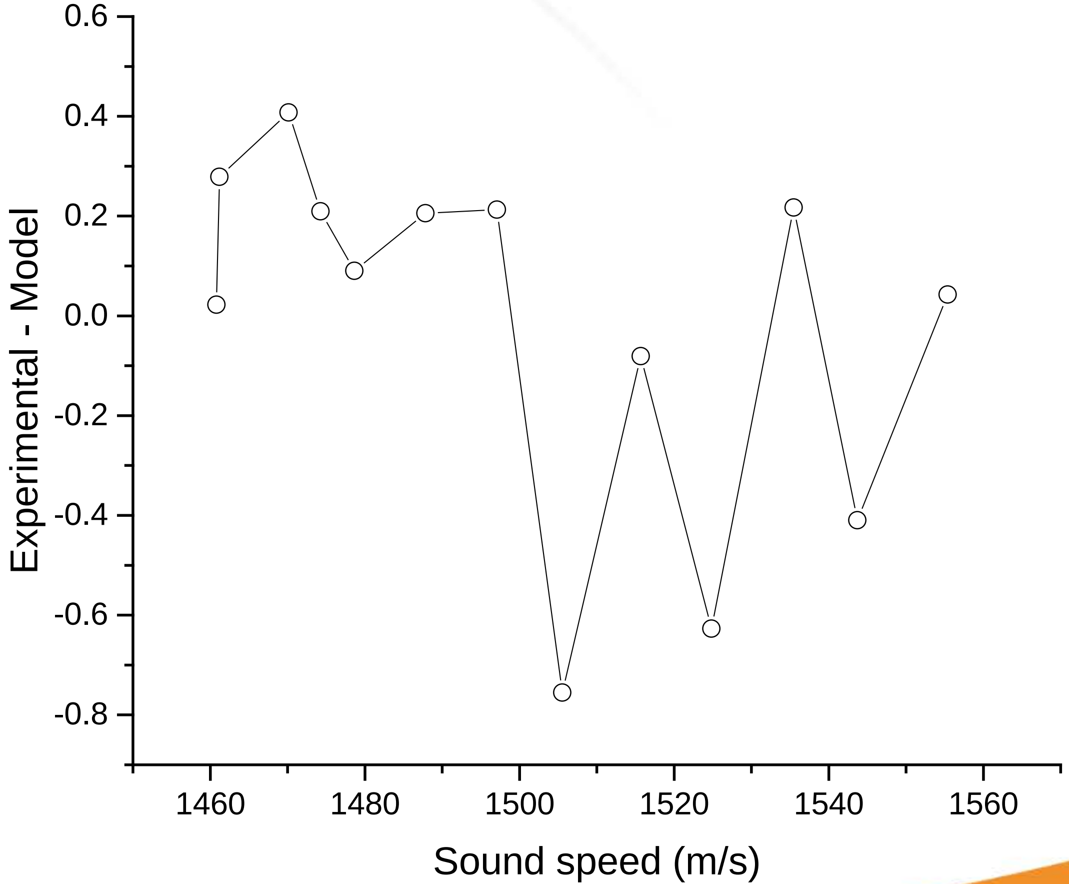
RESIDUAL PLOT!!!

Simple Binary Mixing Rule

Mixture law: Urick model

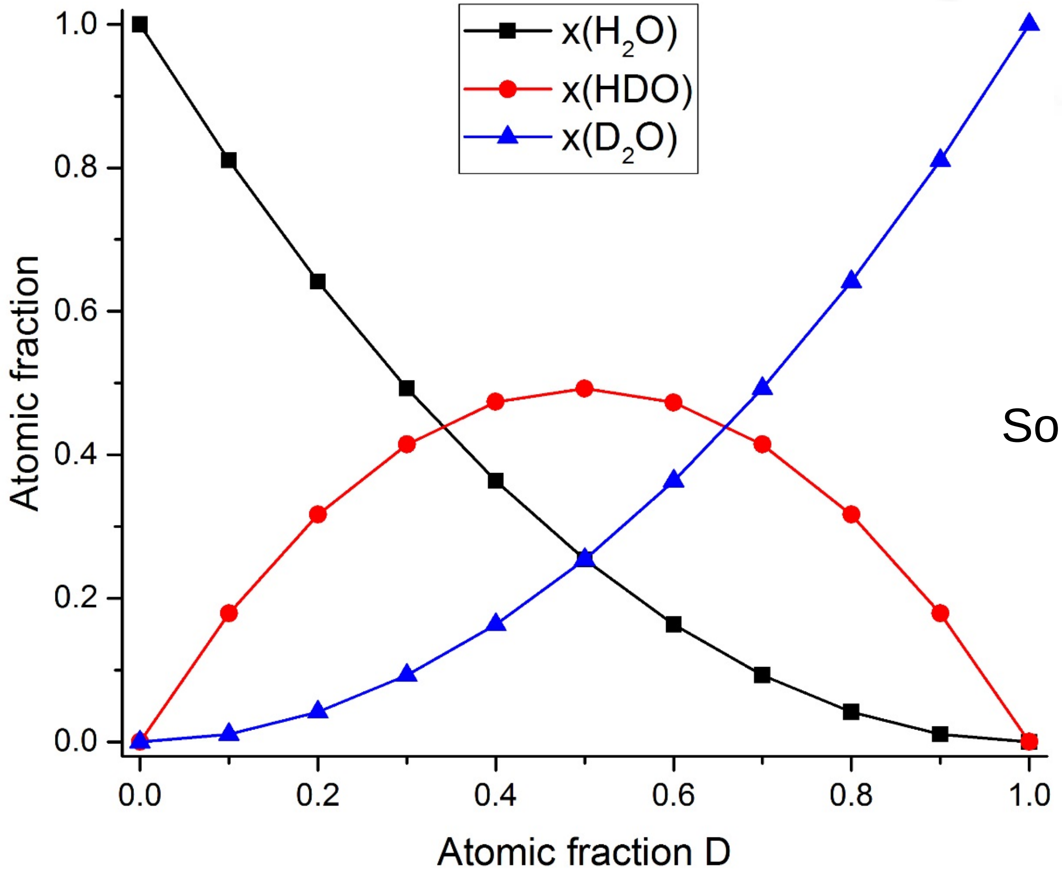


Difference (Experimental – Model)



Heavy Water – 3 Molecule System

*Hydrogen Isotope Disproportionation



Sound speed HDO ???

Submitted a Proposal to NA241 SGTech Call

U.S. DEPARTMENT OF ENERGY

SENSITIVITY LEVEL

Non-invasive acoustic monitoring of D_2O concentration

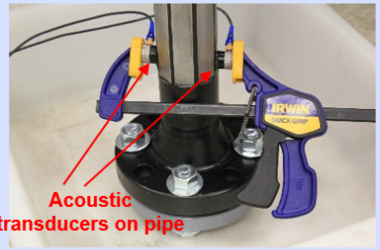
NNSA — OFFICE OF NONPROLIFERATION AND ARMS CONTROL (NPAC) — INTERNATIONAL NUCLEAR SAFEGUARDS

Field portable and process monitoring solutions for heavy water verification

Background/State of the Art

- Current methods: periodic sampling or invasive continuous monitoring
- No persistent monitoring and verification
- Relatively expensive
- Needs significant user interaction
- No other entity works on acoustics approach

Innovation



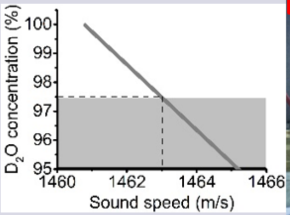
- Use acoustics and clamp-on transducers
- **Noninvasive, unattended, continuous monitoring**
- Preliminary data very promising. Sound speed sensitive to H/D content.

R&R #: 01

Approach, Metrics and Outcomes

MAIN GOAL

- Reduce inspectors presence/increase verification coverage
- Demonstrate functionality in the field on different storage forms (process pipes, drums, tank walls, etc.)



HOW IT WORKS

- Determine accurate sound speed in fluid using Swept Frequency Acoustic Interferometry (SFAI).
- We already demonstrated high precision/accuracy for D_2O concentration, ~ 0.1% (relative) in laboratory.

ASSUMPTIONS, LIMITATIONS & CONSTRAINTS

- Constraints: at low temperatures (5°C), the temperature has to be measured within 0.03°C. However, at high temperatures (70°C), measurements within 0.5°C will suffice.

SENSITIVITY LEVEL: UNCLASSIFIED AND REVIEW & RELEASE NUMBER

Impact

- Safeguards relevance
  - Current approaches do not provide noninvasive continuous monitoring and verification by the IAEA
  - CONOPS 1: man portable tool
  - CONOPS 2: continuous unattended verification
- Long-Term R&D STR-375 LTRD Capability 5/LTRD Milestone 5.6
- IAEA STR-382 Objective: SGTS-001, NDA Techniques, Objective 3
- **Start of FY TRL = TRL5**
- **End of FY TRL (Planned) = TRL6**
- **End of project TRL (Planned) = TRL8**

Goals/Action Plan

- **Planned tasks:**

1 - Portable on-site inspection tool
2 - User-friendly software interface
3 - Continuous unattended monitoring
4 - Field tests and technique refinement

Future FY

- Continuous unattended monitoring
- Field tests and technique refinement

Team

Los Alamos National Laboratory

PI: Cristian Pantea
pantea@lanl.gov, 505-665-7598

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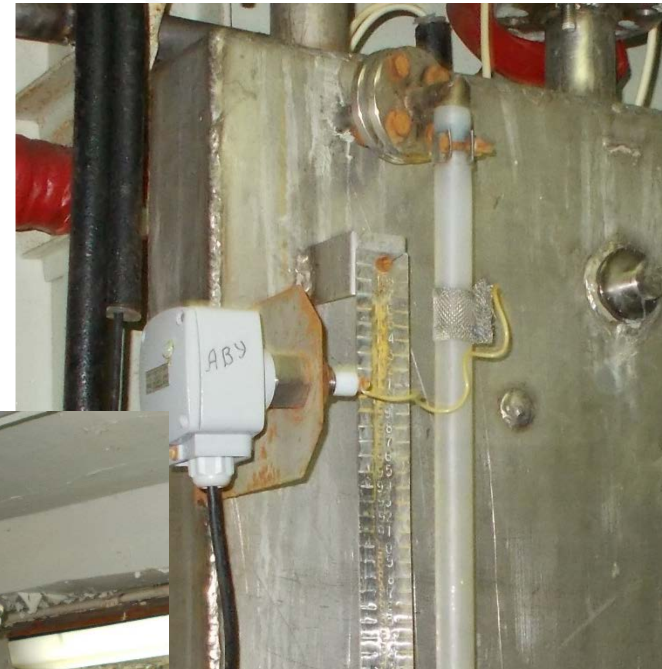
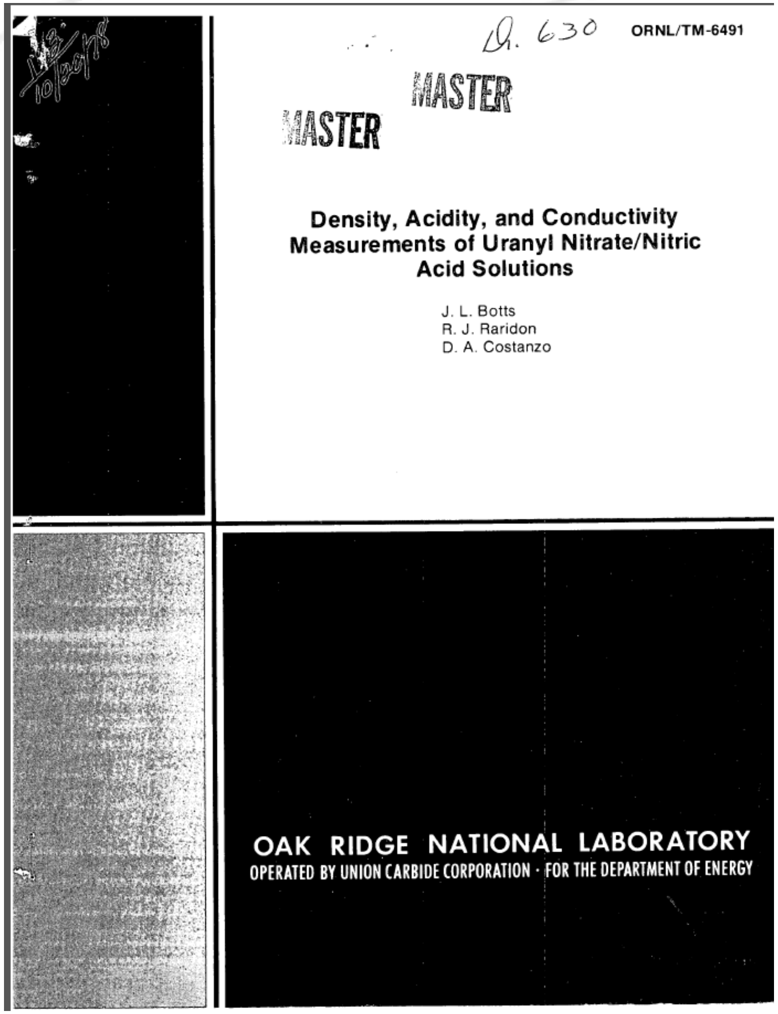
Uranium Solution Monitoring:
Inspired by IAEA Challenge in Kazakhstan



Non-Invasive Acoustic-Based Monitoring of Uranium in Solutions


ORNL/TM-6491

MASTER

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Density, Acidity, and Conductivity Measurements of Uranyl Nitrate/Nitric Acid Solutions

J. L. Botts
R. J. Raridon
D. A. Costanzo

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

The density of each solution used in the experiment was determined by pycnometric measurement to an accuracy of ±0.05%.

The conductivities, i.e., specific conductances, of the experimental solutions were measured using a Radiometer conductivity meter (type CDM3) with a dip-type conductivity cell. The cell constant for the meter was experimentally determined to be 1.00 cm within 1.34%. This meter is equipped with temperature compensation and is capable of measuring conductances from 1.5 microsiemens to 200 millisiemens.

SUMMARY

Conductivity, density, and acidity measurements were made on a series of uranyl nitrate solutions under a number of process conditions of temperature and acidity. It has been found from this study that the acidity and conductivity of the solutions were quite sensitive to the uranium and nitrate concentration, whereas the density is sensitive only to the uranium concentration.

The complex relationships among acidity, conductivity, temperature, density, and concentration were quantified in this study. Computer programs were written to quickly predict or calculate the uranium and nitrate concentrations where (a) the temperature, density, and conductivity or (b) the temperature, density, and pH are known. The use of these programs will allow precise process control to be exercised in the preparation of HTGR recycled fuel particles by the simple monitoring of the density, temperature, and either conductivity or pH of the process solution.

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Non-Invasive Acoustic-Based Monitoring of Uranium in Solutions

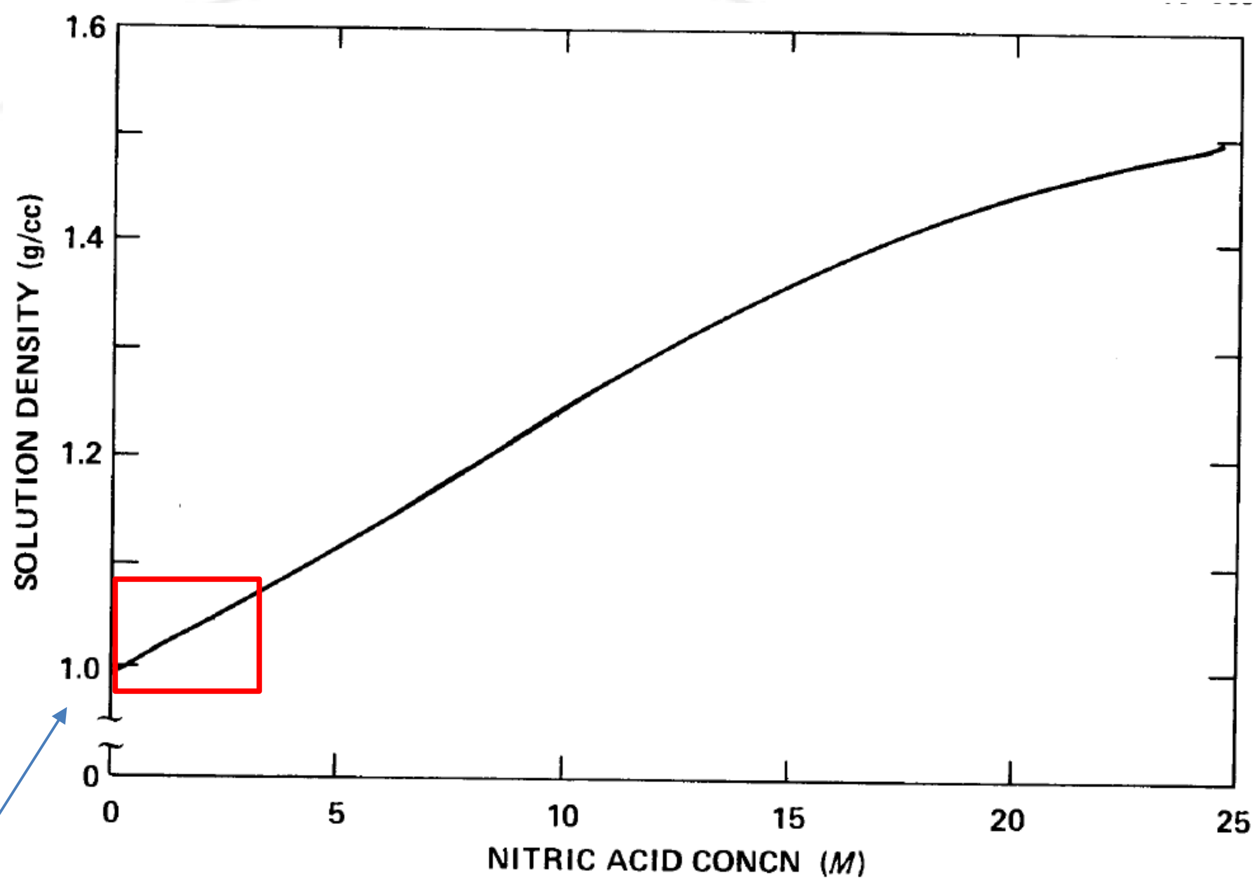


Fig. 2.2. Density of nitric acid solutions as a function of molar concentration at 25°C.

For this proof-of-principle, we investigated the outlined area above.

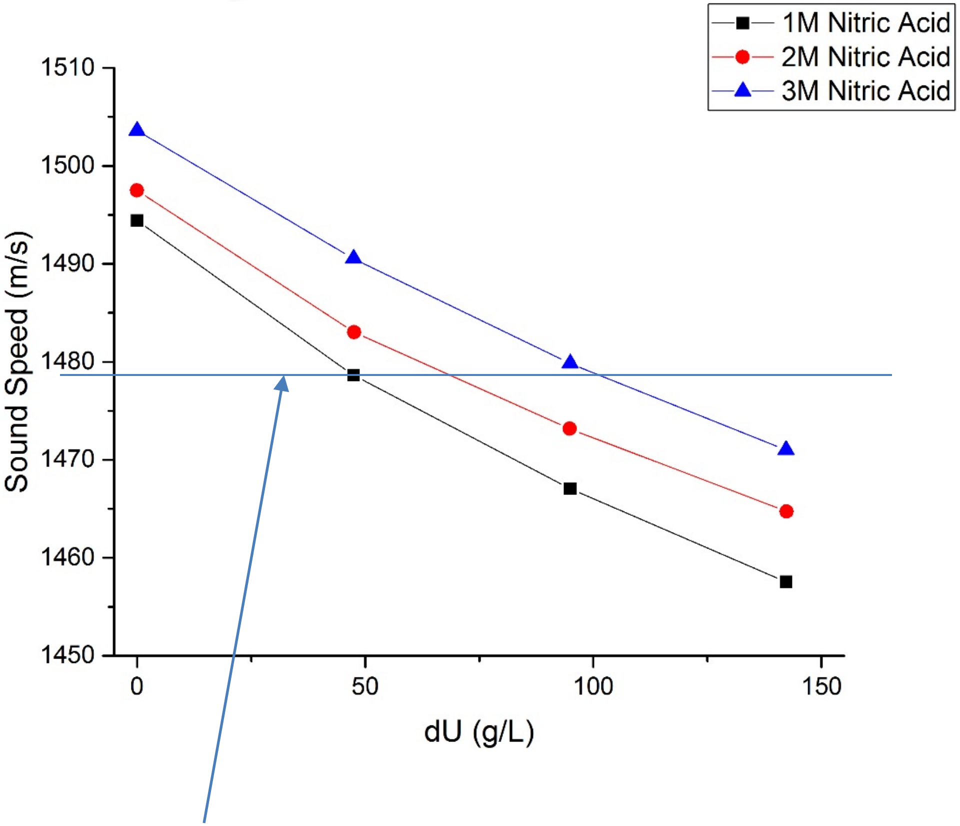
Non-Invasive Acoustic-Based Monitoring of Uranium in Solutions

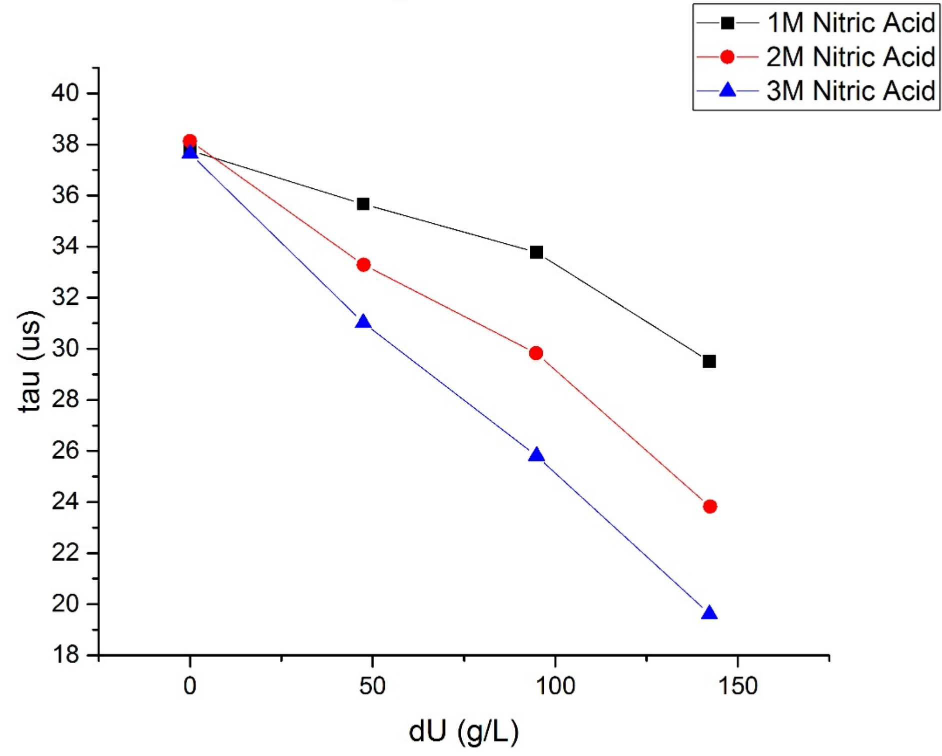
The following solutions were prepared by Greg Wagner (C-PCS) and Marianne Wilkerson (C-DO)

1	Sample number	HNO_3 Conc.	Sample vol	g of $UO_2(NO_3)_2.6H_2O$ (UNH)	g DU	g dU/g UNH	DU g/l	UNH g/l
2	1	1M	24ml	0	0.0000	0.4741	0.0	0.0
3	1001	1M	24ml	2.4019	1.1387	0.4741	47.4	100.1
4	2001	1M	24ml	4.8070	2.2790	0.4741	95.0	200.3
5	3001	1M	24ml	7.2005	3.4138	0.4741	142.2	300.0
6	2	2M	24ml	0	0.0000	0.4741	0.0	0.0
7	1002	2M	24ml	2.4079	1.1416	0.4741	47.6	100.3
8	2002	2M	24ml	4.8001	2.2757	0.4741	94.8	200.0
9	3002	2M	24ml	7.2086	3.4176	0.4741	142.4	300.4
10	3	3M	24ml	0	0.0000	0.4741	0.0	0.0
11	1003	3M	24ml	2.4022	1.1389	0.4741	47.5	100.1
12	2003	3M	24ml	4.8047	2.2779	0.4741	94.9	200.2
13	3003	3M	24ml	7.2000	3.4135	0.4741	142.2	300.0
14				**Total g of dU**	**20.4967**			

Non-Invasive Acoustic-Based Monitoring of Uranium in Solutions

1 measurement -> 2 variables
Sound speed and Attenuation





Sound speed alone does not uniquely identify U concentration

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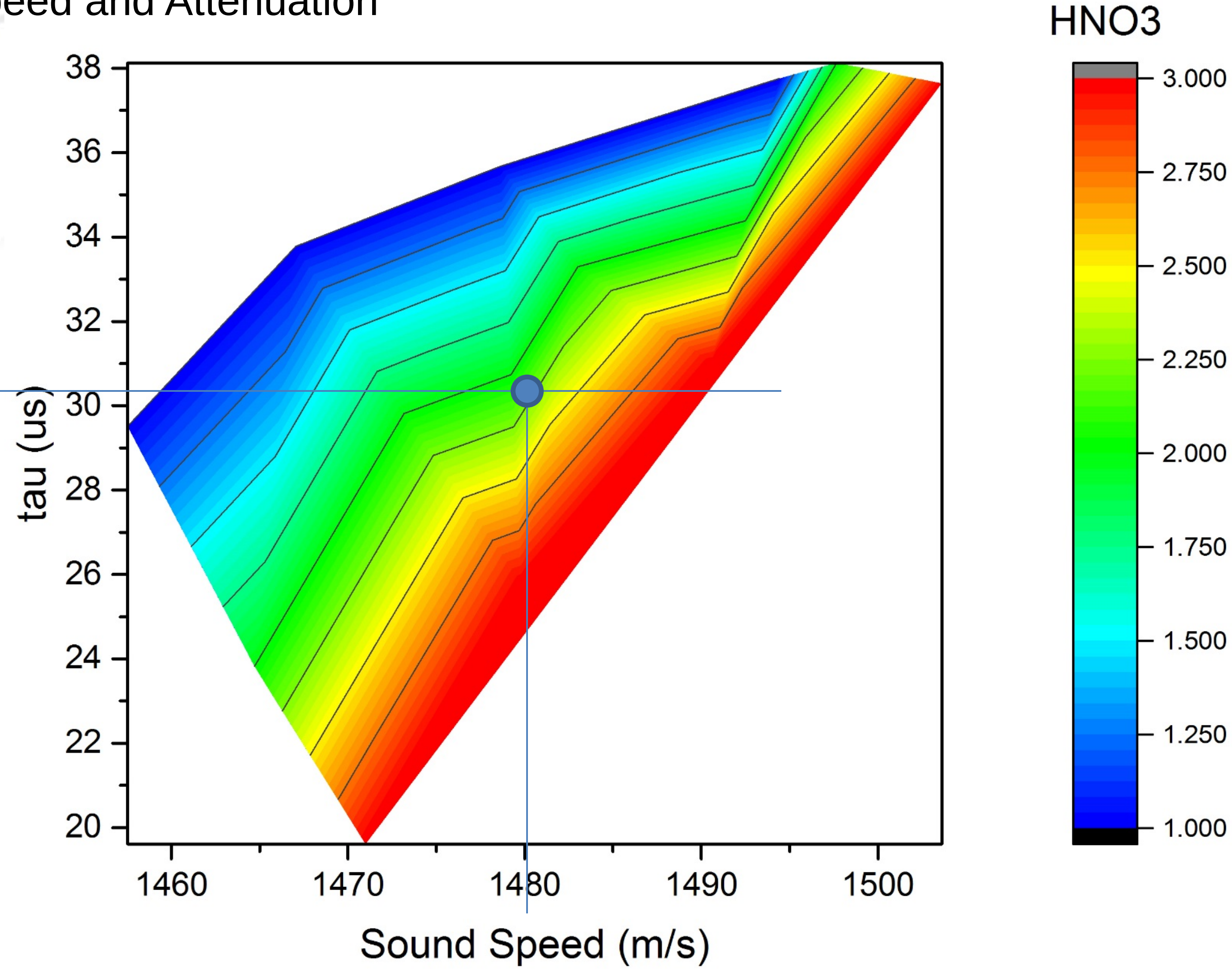
1 measurement -> 2 variables
Sound speed and Attenuation



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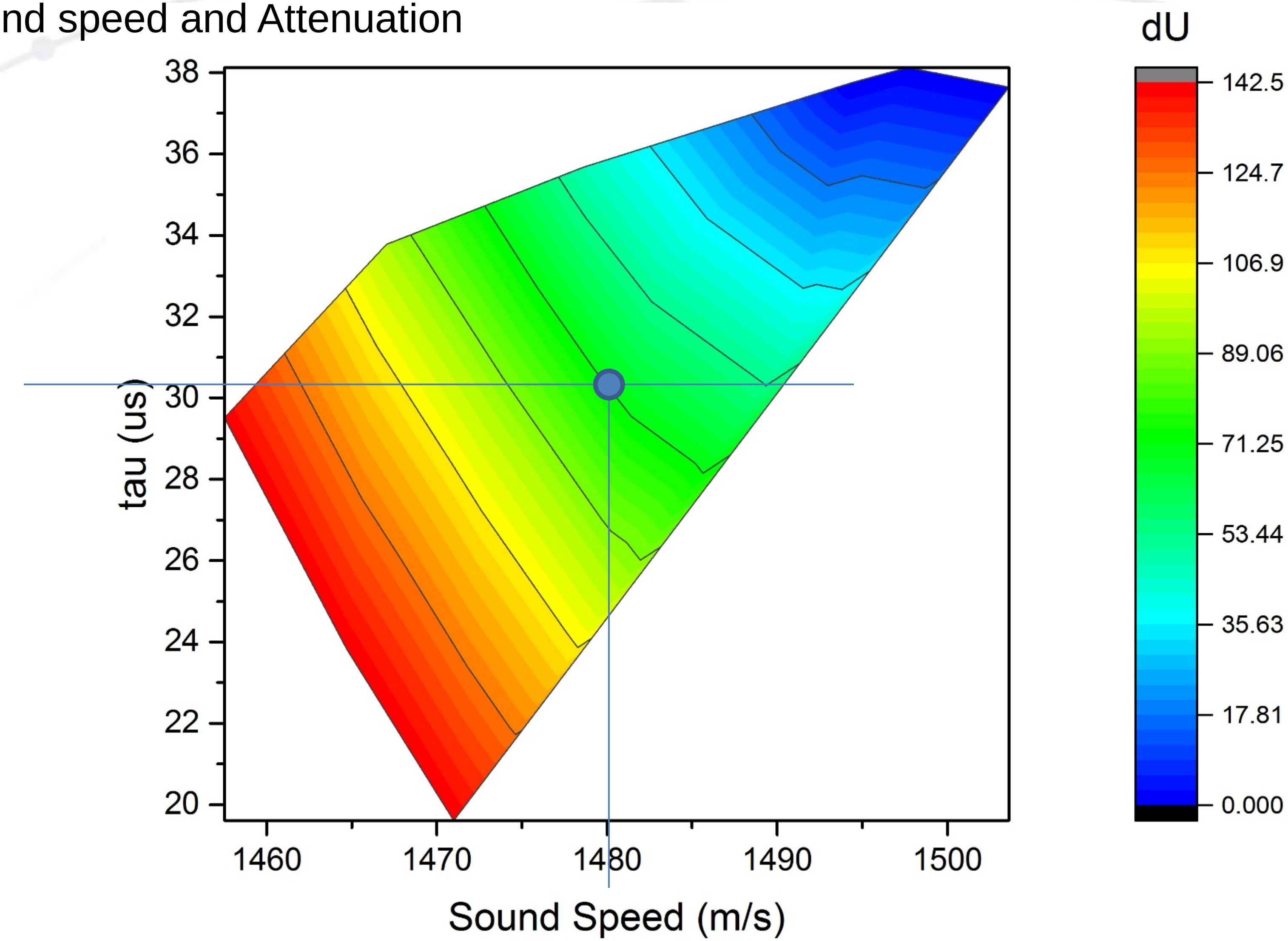
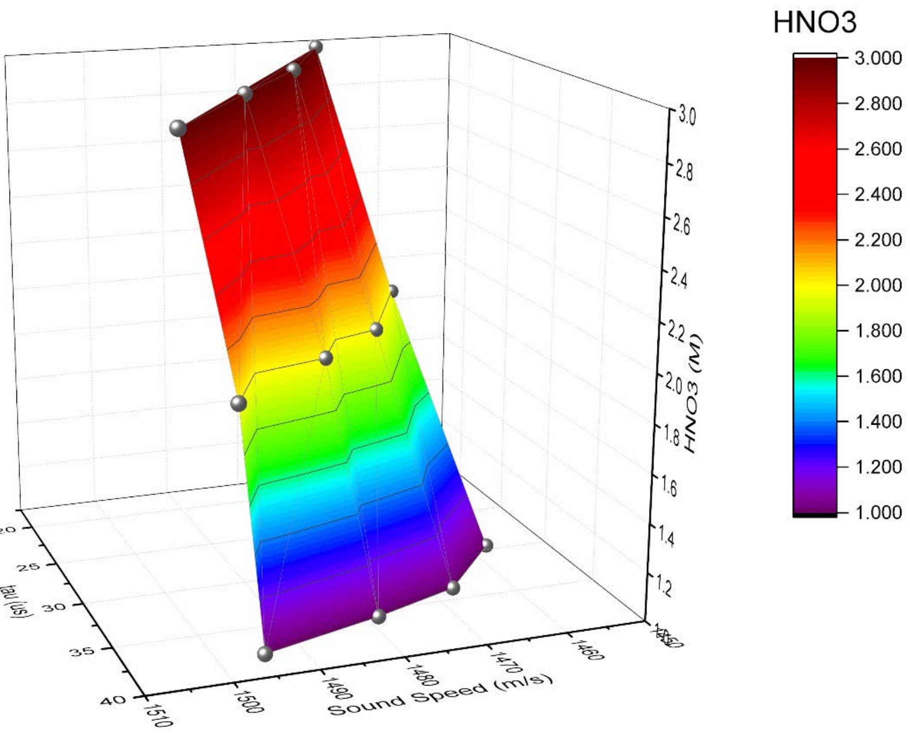
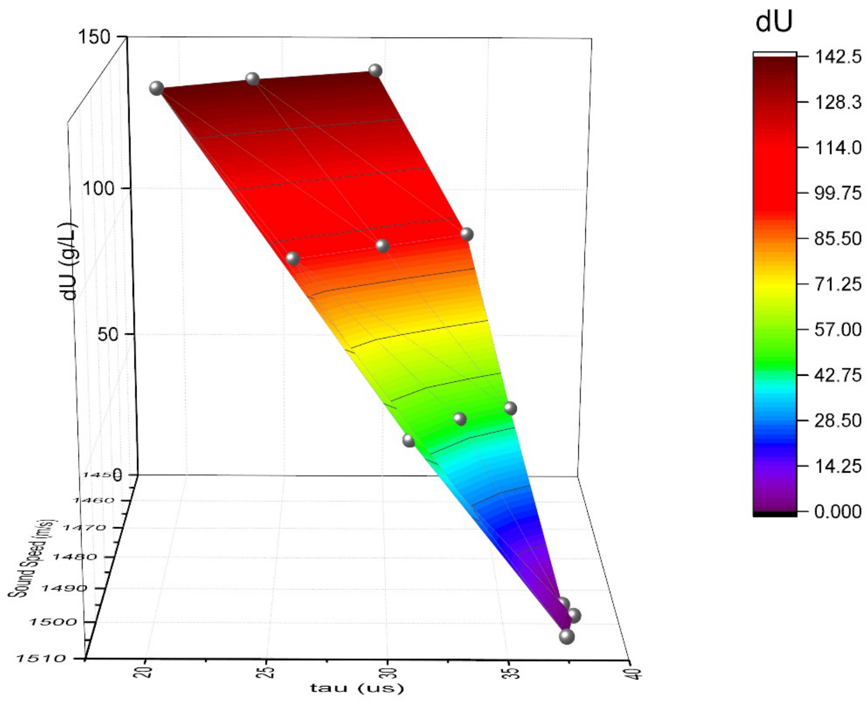
Sound speed and Attenuation



Non-invasive acoustic-based monitoring of Uranium in Solutions

1 measurement -> 2 variables
Sound speed and Attenuation





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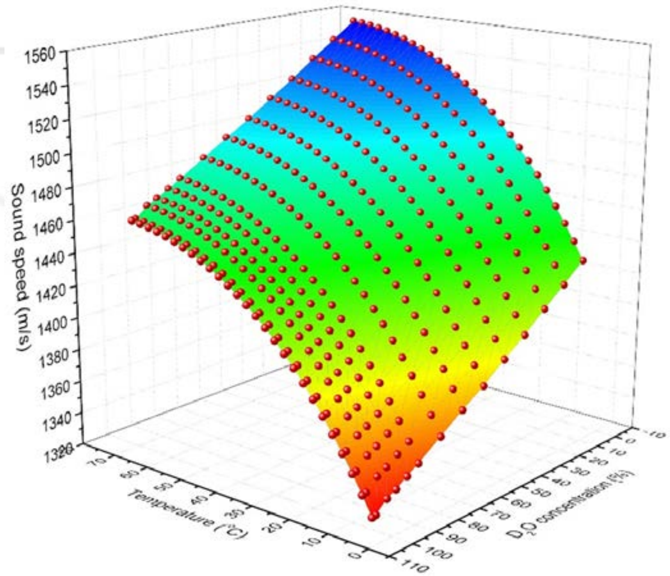
Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

Summary

- Developed methodology for in-situ and onsite verification of D2O inventory
- New method for U process solution verification - Disruptive for process monitoring!!!
- Simple, low cost, modest electronics, easy deployable



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