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Title: Non-invasive acoustic-based monitoring of uranium in solution and H/D ratio

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

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Non-invasive acoustic-based monitoring of uranium in solution and H/D ratio

Cristian Pantea, Christopher Beedle, Dipen Sinha, Rollin Lakis

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Pathfinder project

- Primary objective:

Adapt existing non-invasive acoustic techniques (Swept-Frequency Acoustic Interferometry and Gaussian-pulse acoustic technique) for the purpose of demonstrating the ability to quantify U or H/D ratios in solution.

A successful demonstration will provide an easily implemented, low cost, and non-invasive method for remote and unattended uranium mass measurements for International Atomic Energy Agency (IAEA).

Justification Uranium in solutions

- Solutions of uranyl nitrate in nitric acid are common in several nuclear fuel cycle operations including: uranium mining and milling; fuel fabrication; scrap recovery and reprocessing.

- Different operators and processes use solutions that span a wide range of nitric acid and uranium concentrations. Previous approaches have used the combination of solution density and electrical conductivity to determine nitric acid and uranium concentrations. While reasonably effective, current process monitoring or in-situ methods for density determination require complex and troublesome triple-bubblers also referred to as electro-manometers. These systems require significant care and have been successfully implemented in only sophisticated facilities.

Justification Uranium in solutions

- Acoustic methods may provide a better resolved and more unique uranium/nitric acid phase space.
- Additionally, these methods require only modest electronics (already demonstrated for other metering applications) and reliable electrical connections. This is a significant enhancement over electro-manometer techniques.
- Customers include US DOE and DOS programs. This work could have immediate and important impacts for IAEA measurement challenges in the Republic of Kazakhstan.

Justification H/D determination

- Current methods for H/D determination require periodic sampling and analysis. This approach does not provide the opportunity for continuous monitoring and verification by the IAEA and is relatively expensive and inefficient compared to the potential implementation of real-time, online verification by acoustic methods.

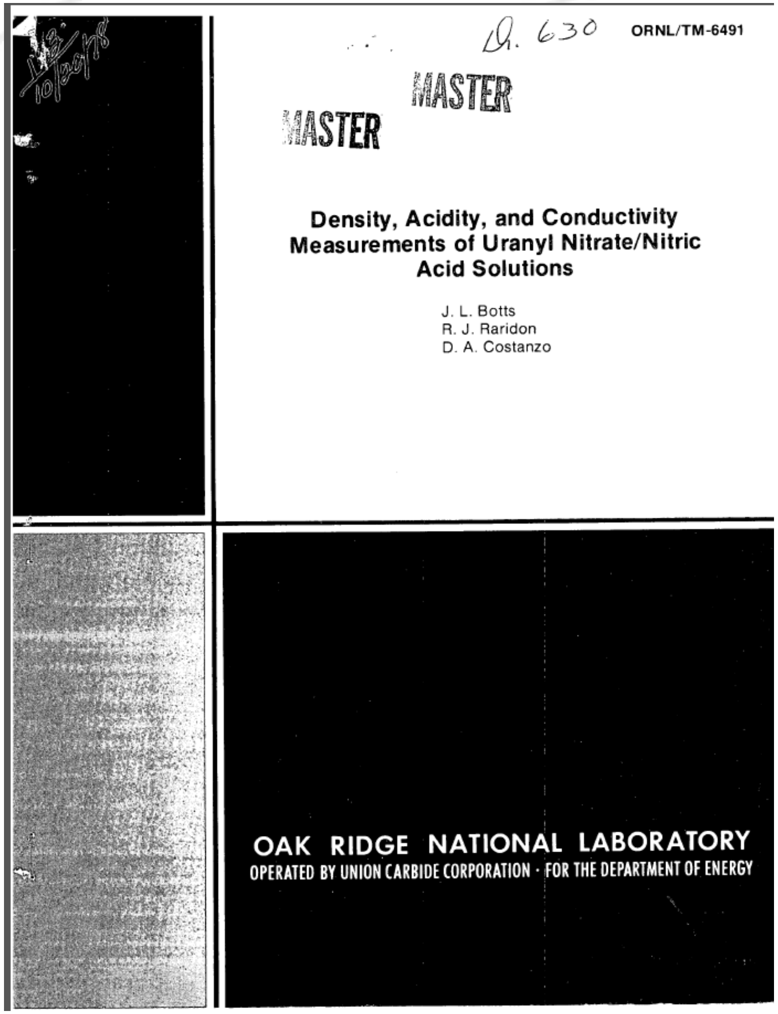
Project scope

- Adaptation of a well-established technique, Swept-Frequency Acoustic Interferometry (SFAI), developed by our team for solution concentration measurement in a noninvasive manner.
- This technique uses ultrasound propagation through a fluid inside any vessel or pipe over a wide frequency range (1-25 MHz) to characterize the fluid.
- The fluid physical properties determined in real-time include sound speed, sound absorption, acoustic nonlinearity, density, and viscosity.
- Multiple properties allow a robust determination of fluid solution concentration although only sound speed, sound attenuation and density may be sufficient. Typical measurement time is less than 1 second.
- The demonstration project will utilize hardware and software techniques previously developed for multi-phase metering of liquid/gas combinations, to demonstrate relevance for these new mission applications.

Deliverables

- At the end of the Pathfinder project we will provide a demonstration of a non-invasive acoustic-based concept for determining density and concentrations of uranium solutions (nitrate and nitric acid).
- Solution density and concentrations of constituents will be determined from acoustic measurements, such as fluid sound speed, acoustic impedance, and sound attenuation, for specific mixtures of nitrate and nitric acid.
- These values will be compared with the ones obtained using traditional analytical techniques. The H/D demonstration will result in a quantitative assessment of the ability of the technique to meet JCPOA monitoring requirements.

Non-invasive acoustic-based monitoring of Uranium in Solutions


ORNL/TM-6491

MASTER

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.

Non-invasive acoustic-based monitoring of Uranium in Solutions

The following solutions were prepared by Greg Wagner in C-PCS

1	Sample number	HNO_3 Conc.	Vol. of sample	g of $UO_2(NO_3)_2.6H_2O$ (UNH)	g of Depleted Uranium
2	1	1M	24ml	0	0.0000
3	1001	1M	24ml	2.4019	1.1387
4	2001	1M	24ml	4.8070	2.2790
5	3001	1M	24ml	7.2005	3.4138
6	2	2M	24ml	0	0.0000
7	1002	2M	24ml	2.4079	1.1416
8	2002	2M	24ml	4.8001	2.2757
9	3002	2M	24ml	7.2086	3.4176
10	3	3M	24ml	0	0.0000
11	1003	3M	24ml	2.4022	1.1389
12	2003	3M	24ml	4.8047	2.2779
13	3003	3M	24ml	7.2000	3.4135
14				**Total g of dU**	**20.4967**

An IWD was approved for work with Uranyl solutions in NEN-1.

Final touches needed to ensure there are no leaks from the SFAI cell.

Will start measurements soon.

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

- Context: There is an urgent need for real-time monitoring of the hydrogen /deuterium ratio (H/D) for heavy water production monitoring.

- Based upon published literature, sound speed is sensitive to the deuterium content of heavy water and can be measured using existing acoustic methods to determine the deuterium concentration in heavy water solutions.

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

- Context: There is an urgent need for real-time monitoring of the hydrogen /deuterium ratio (H/D) for heavy water production monitoring. Based upon published literature, sound speed is sensitive to the deuterium content of heavy water and can be measured using existing acoustic methods to determine the deuterium concentration in heavy water solutions.

- Primary objective: Adapt existing non-invasive acoustic techniques (Swept-Frequency Acoustic Interferometry and Gaussian-pulse acoustic technique) for the purpose of demonstrating the ability to quantify H/D ratios in solution. A successful demonstration will provide an easily implemented, low cost, and non-invasive method for remote and unattended H/D ratio measurements with a resolution of less than 0.2% vol.

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

- We propose an approach that can lead to a precision and accuracy of better than ± 0.2%, volumetric.
- A quick literature search leads to 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.)
- All these require drawing of a sample, elaborate sample preparation, time consuming, depends on user interpretation.
- Our approach consists of a clamp-on type device that can accurately measure D_2O concentration in real-time in real settings.

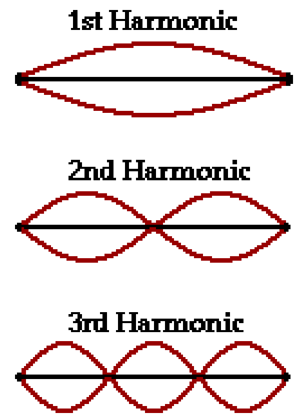
Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

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

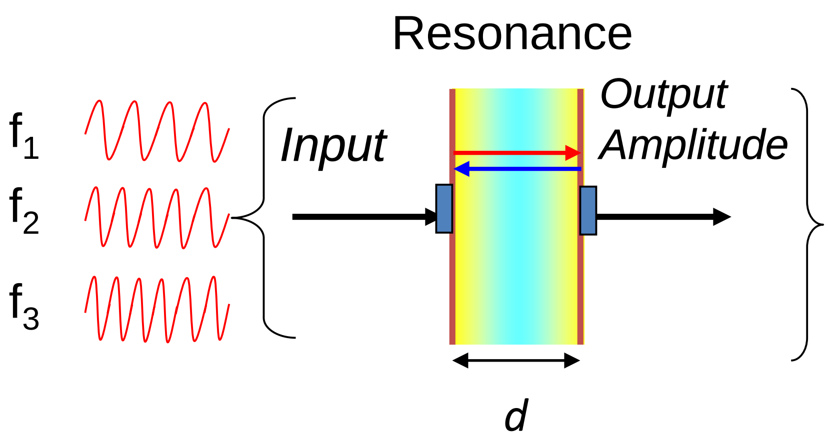
Resonance occurs when:

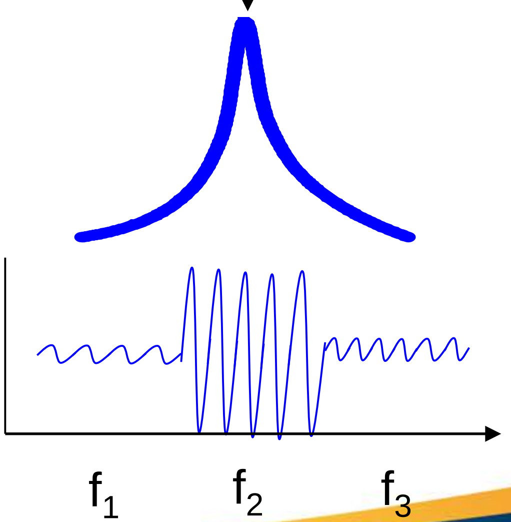
$$d = n.(\lambda/2)$$

n=1, 2, 3…
λ=wavelength



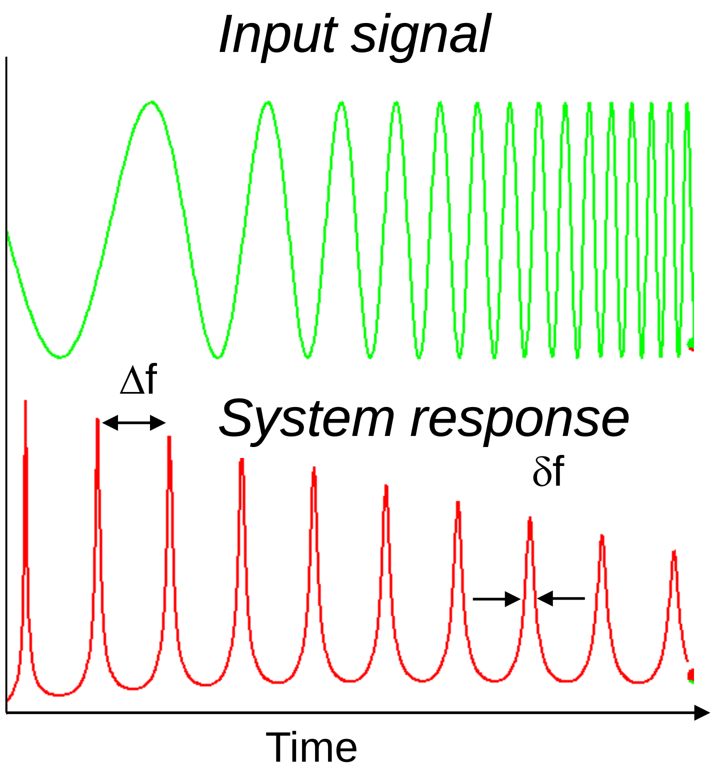
Examples of standing wave when resonance occurs





Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

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



Sound speed = $2d\Delta f$

Sound absorption ✪ δf

Δf =frequency spacing

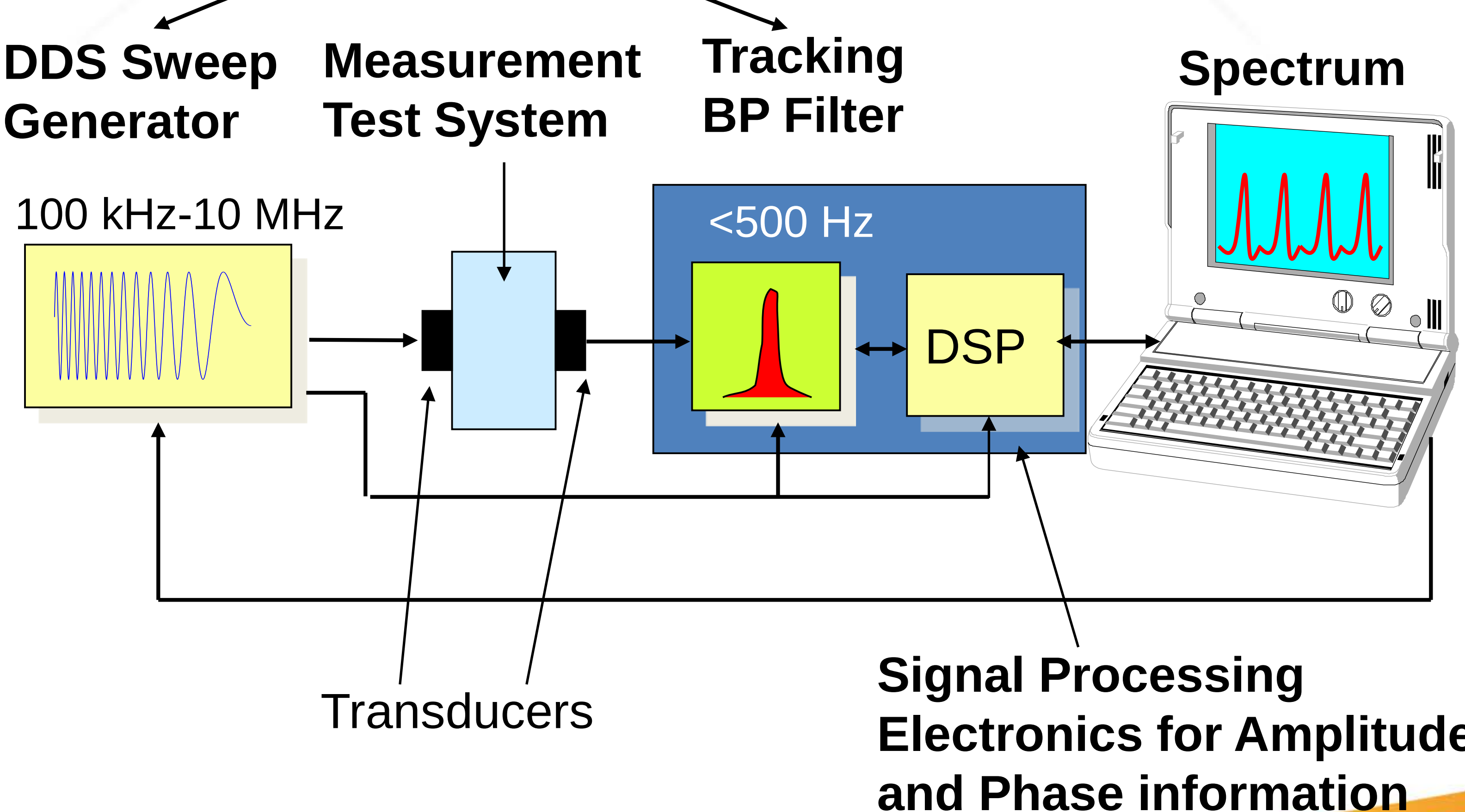
δf =peak width

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

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

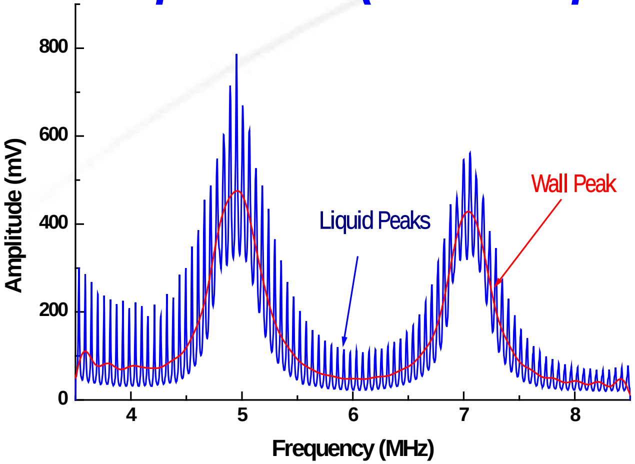
SFAI Instrumentation Basics

The special electronics makes everything possible

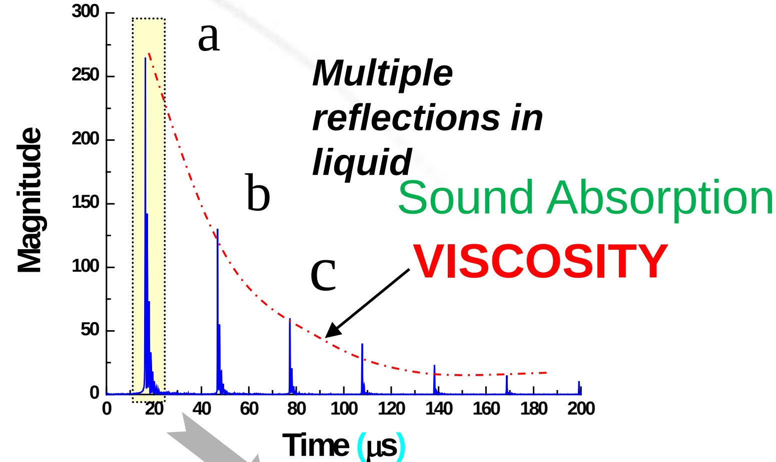


Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

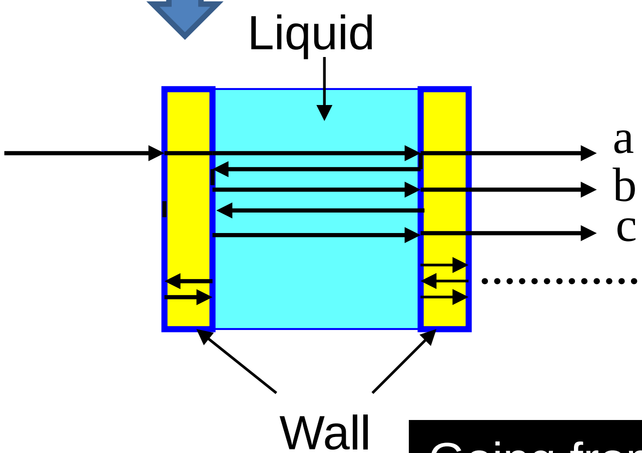
SFAI Spectrum (wide frequency)

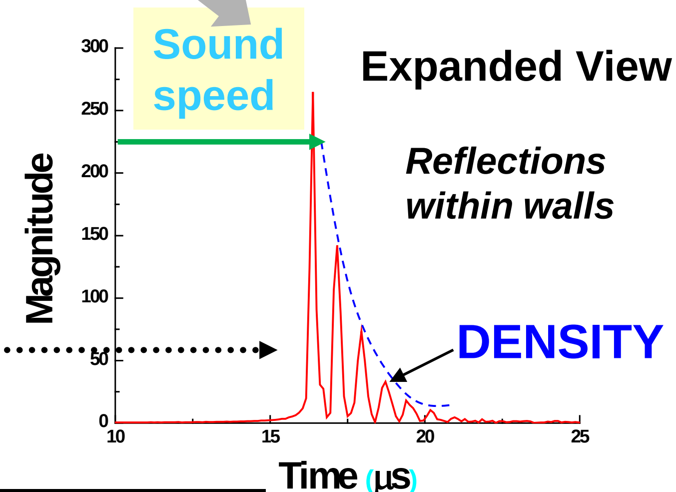


FFT



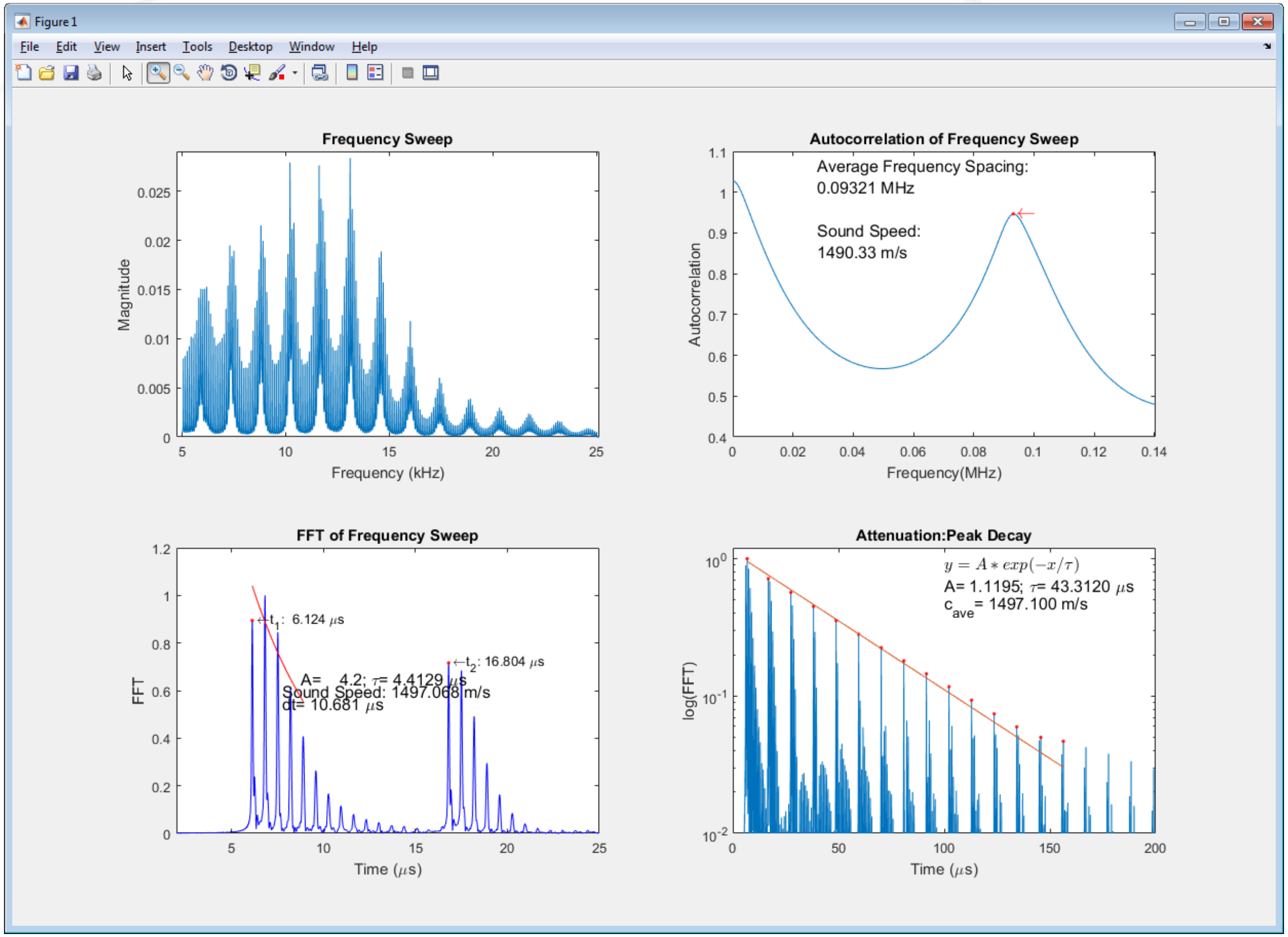
Equivalent:





Going from Frequency to Time

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio



Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

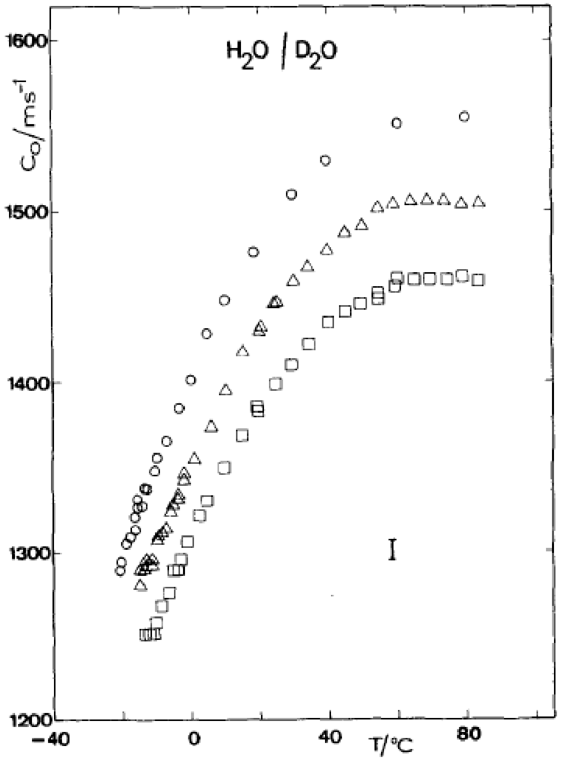
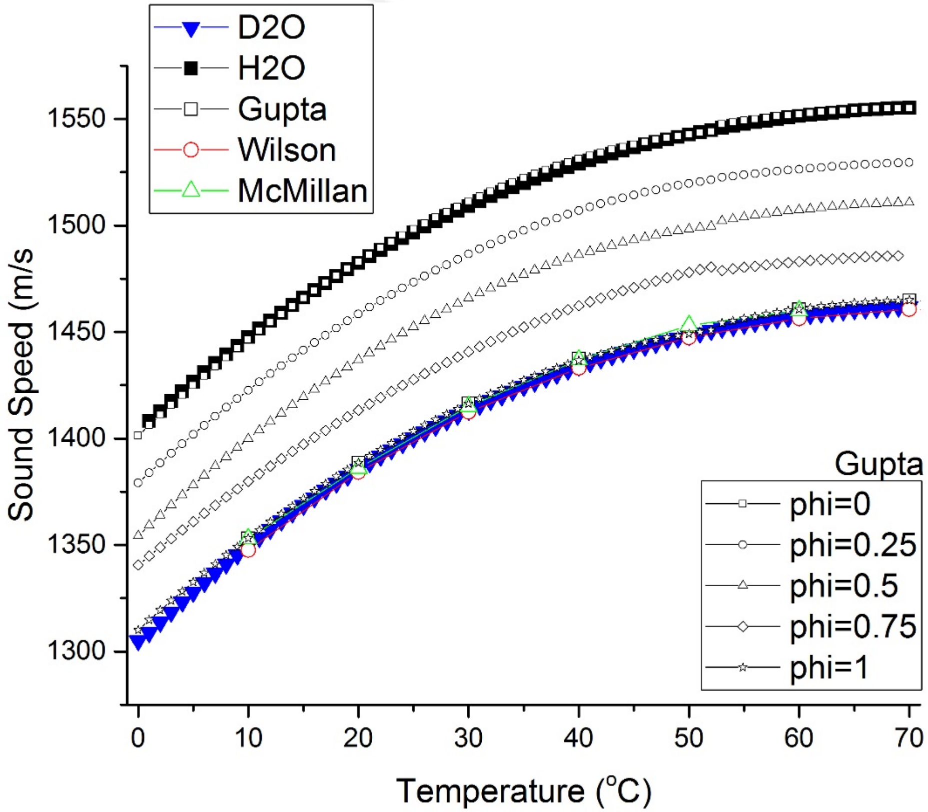


FIG. 1. Sound velocity vs temperature in ○: pure H_2O; □: pure D_2O; Δ: $(H_2O)_{0.525}(D_2O)_{0.475}$ solution.

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

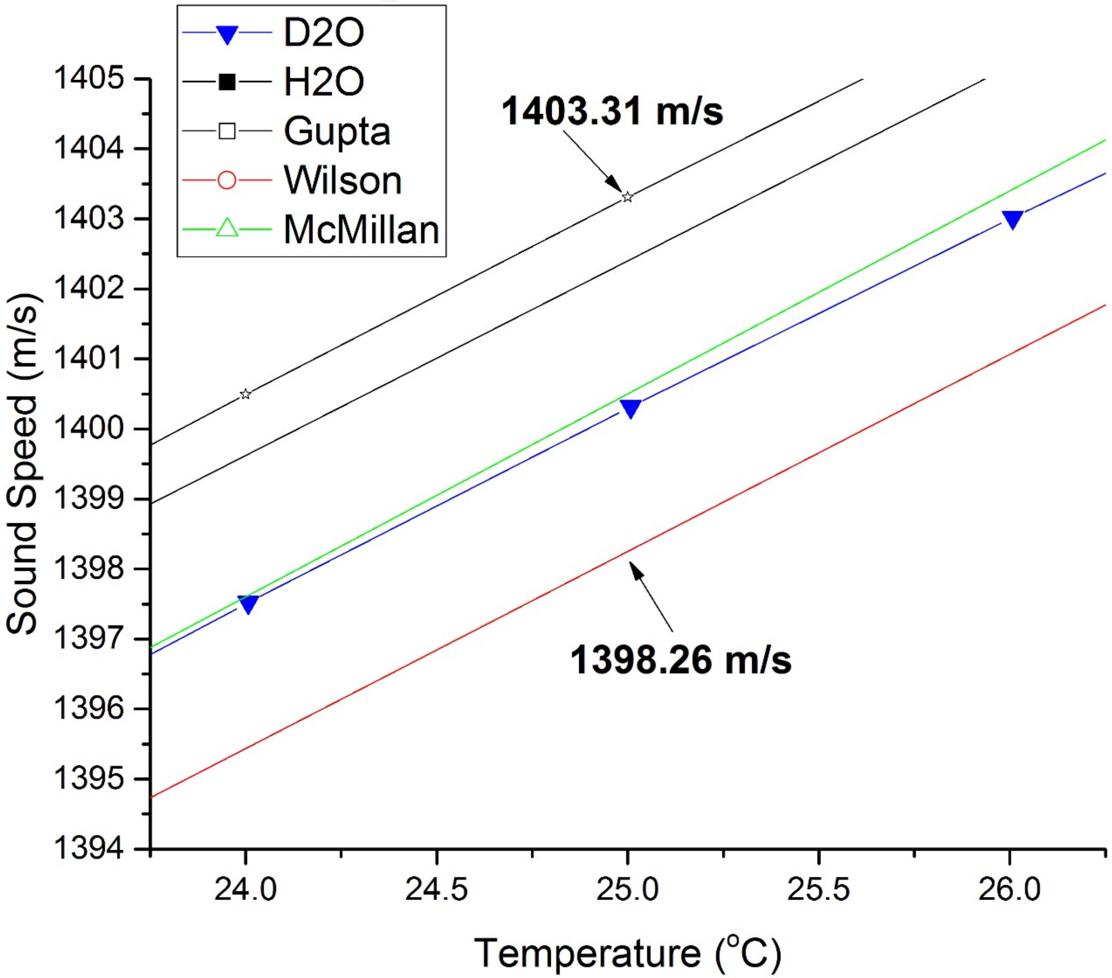


Gupta, J. Chem. Thermodynamics 1976, 8,627
Wilson, JASA 1961, vol 33, no. 3, 314
McMillan, JASA 1947, vol 19, no. 6, 956

Old data
Large scatter

D_2O purity not well known

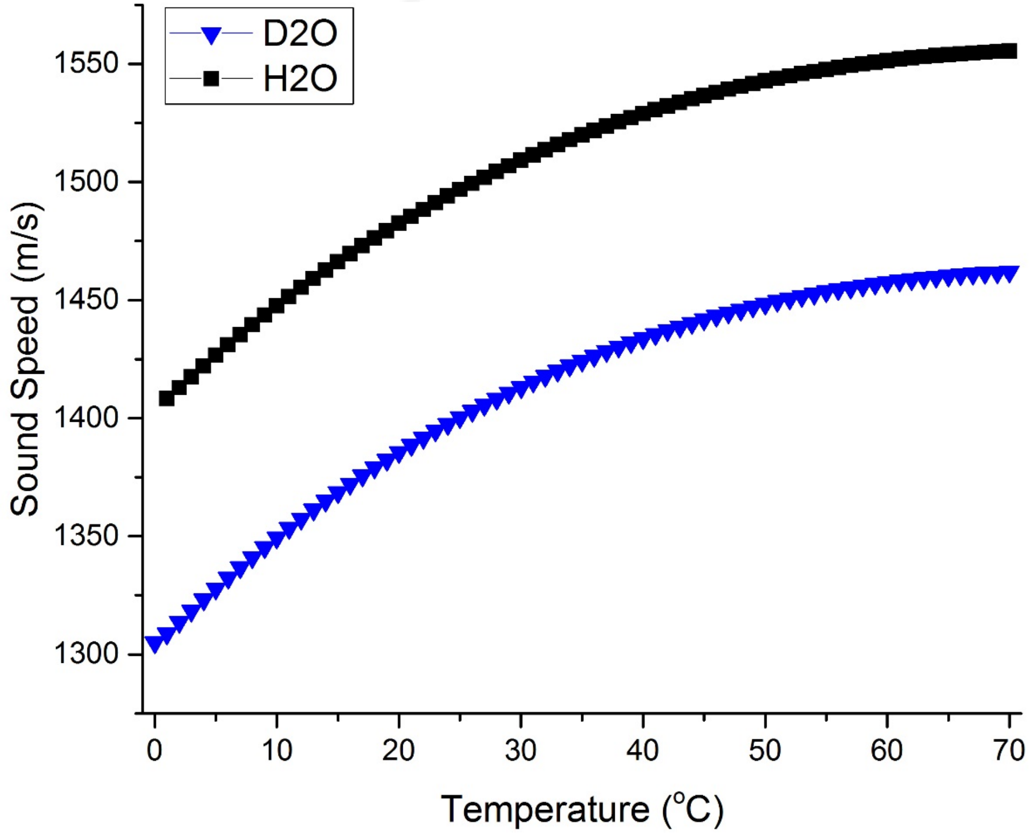
Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio



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

*Wilson used 99.82% D_2O

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio



The difference in sound speed between pure D_2O and pure H_2O is approximately 100 m/s

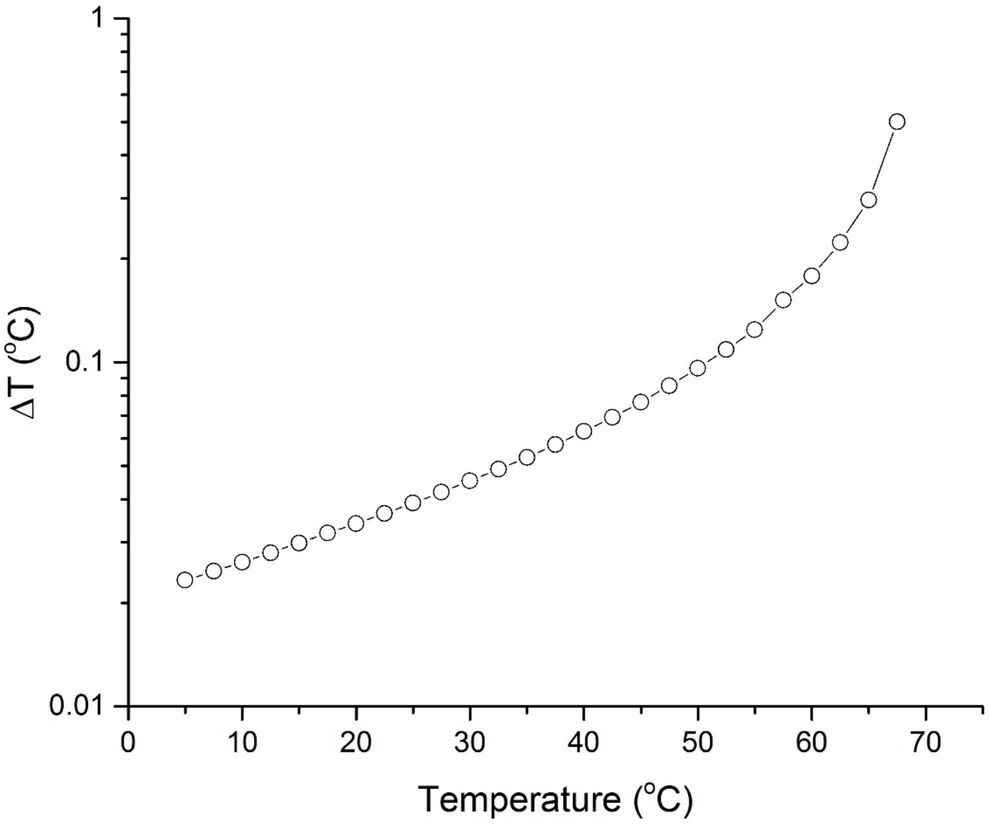
The sound speed can be measured very precisely and accurately, to the first decimal point

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

nuclear reactor grade:
99.75–99.98% deuterium enrichment

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

Temperature effect:



In order to measure a sound speed with a precision better than **0.1 m/s**, the temperature has to be known to better than:

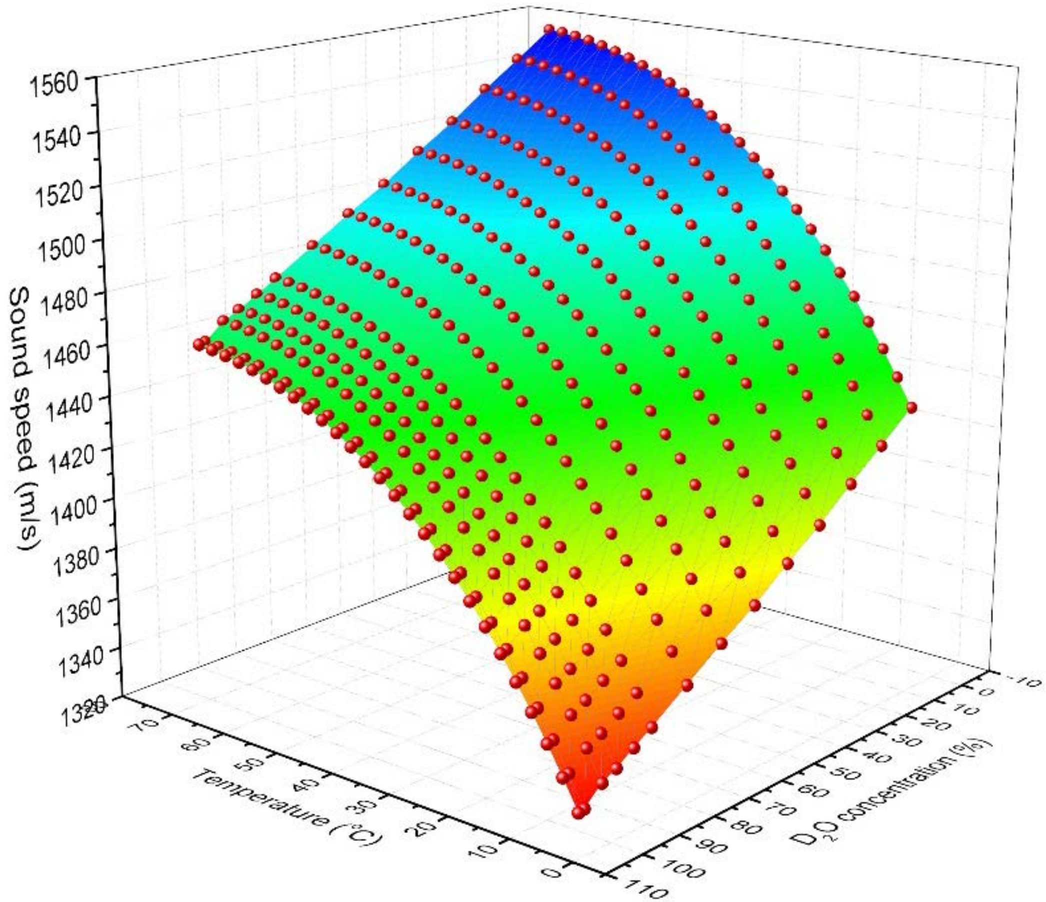
0.02°C @ 5°C

0.04°C @ 25°C

0.5°C @ 70°C

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

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



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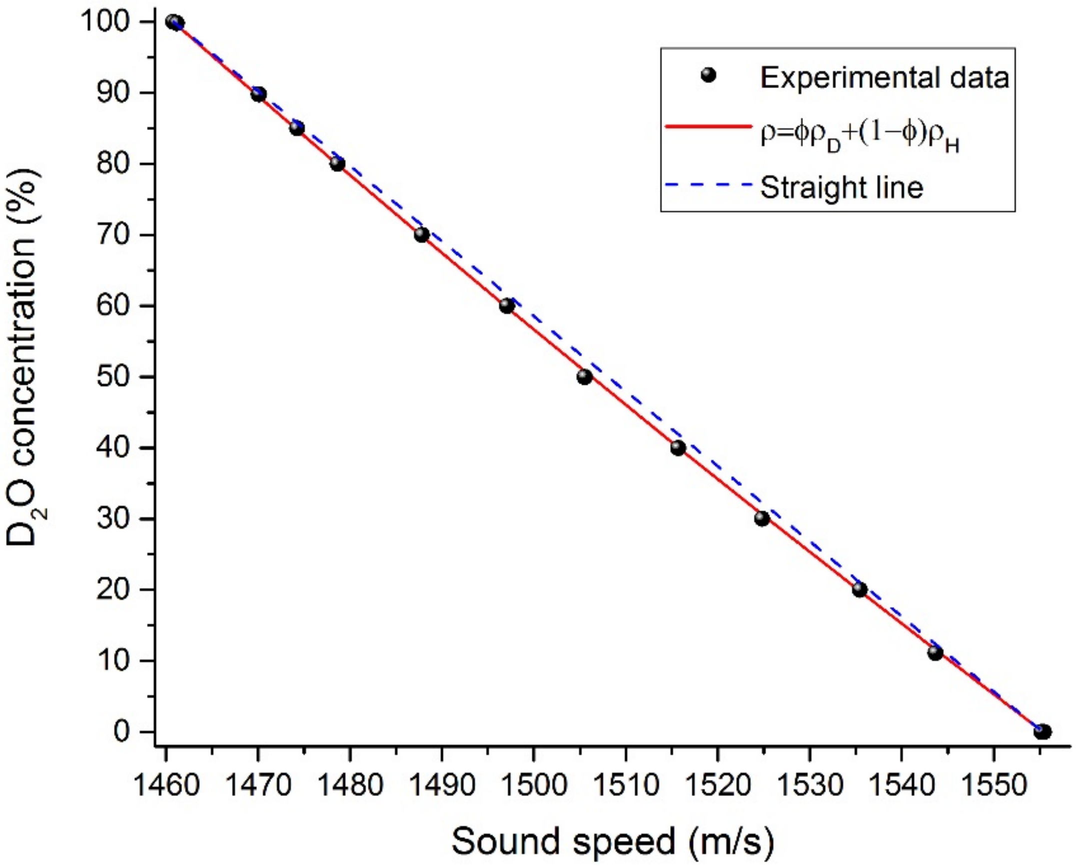
Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

Mixture law: Urick model



Simple linear combination based on the volume fraction φ:

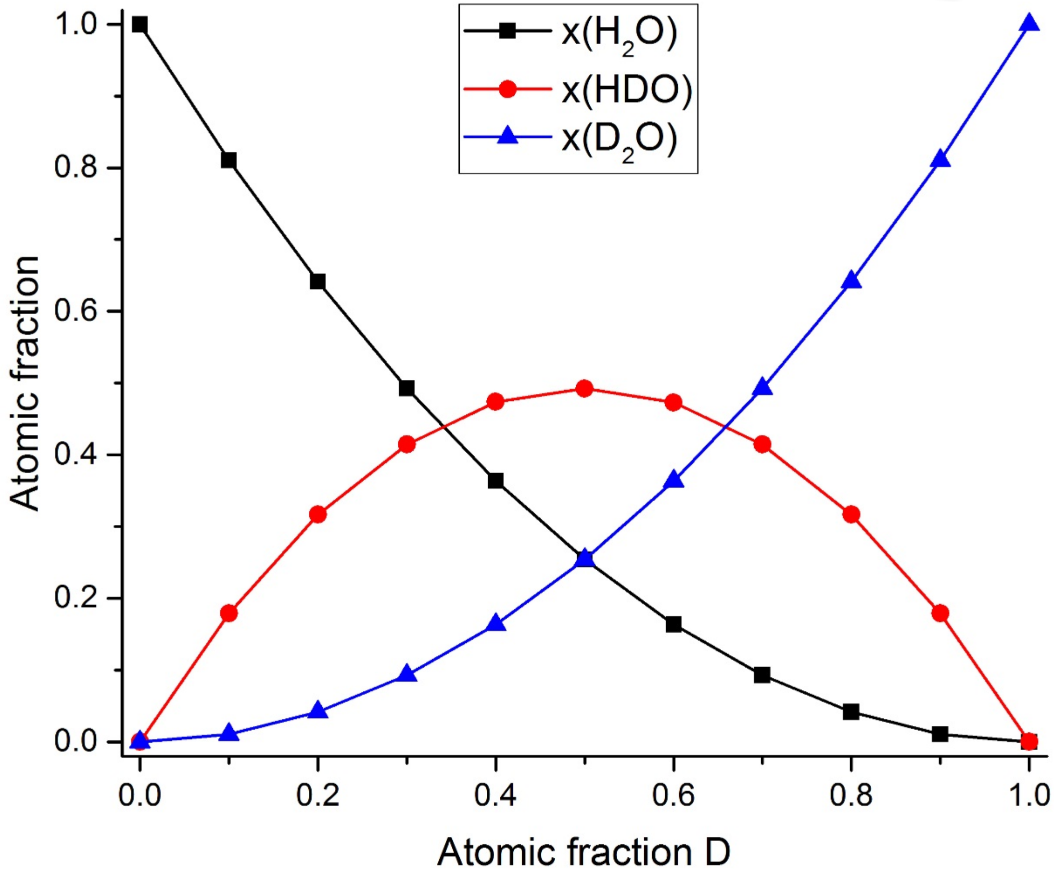
$\rho = \varphi \rho_D + (1-\varphi)\rho_H$,

ρ_D - density of pure D_2O

ρ_H - density of pure H_2O

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio

*Hydrogen Isotope Disproportionation



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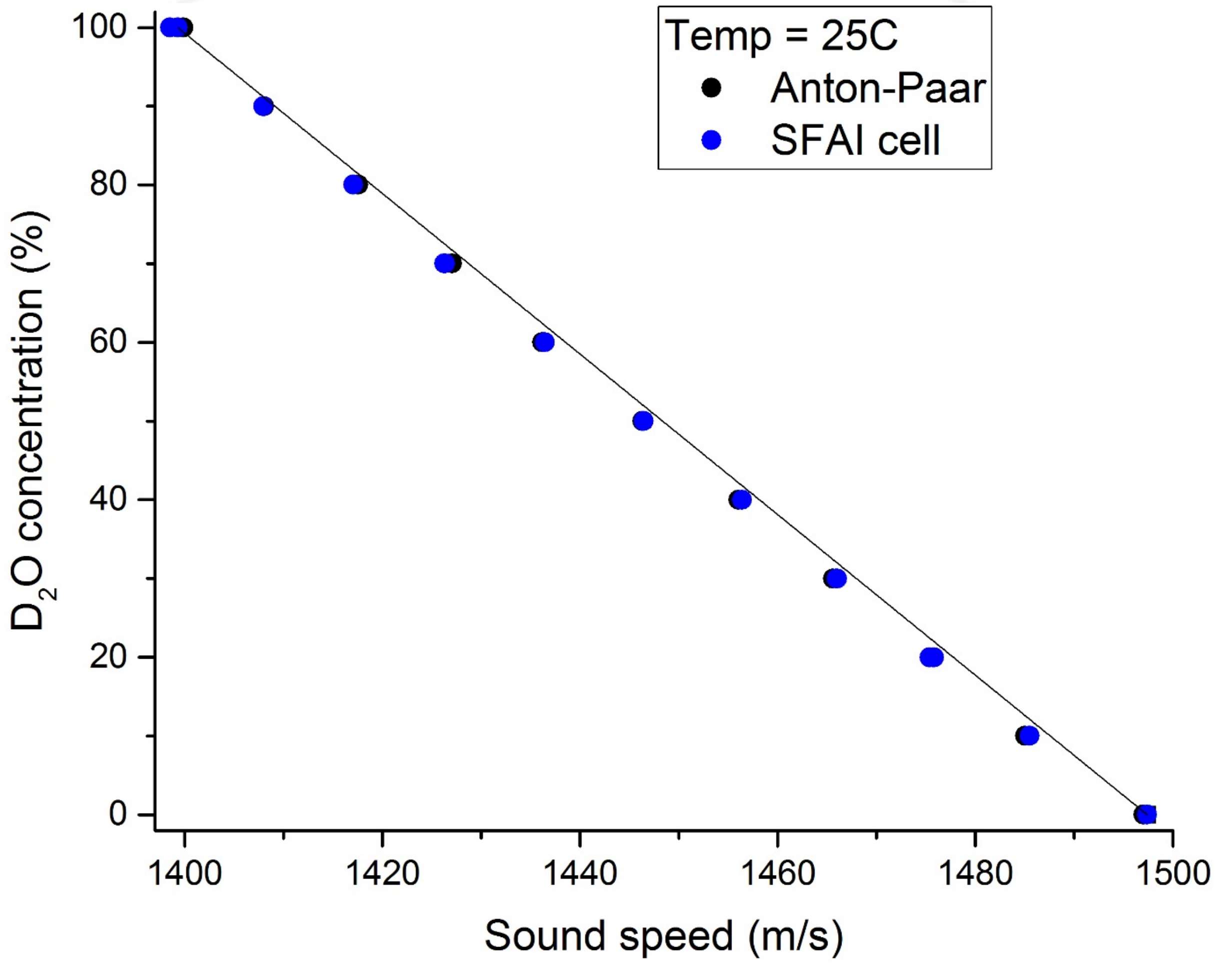

Non-invasive acoustic-based monitoring of Hydrogen/Deuterium ratio