Transient thermal conductivity/ diffusivity measurements

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17 July 2024

Workshop on Measurement and Analysis of Thermochemical and Thermophysical Properties of Molten Salts

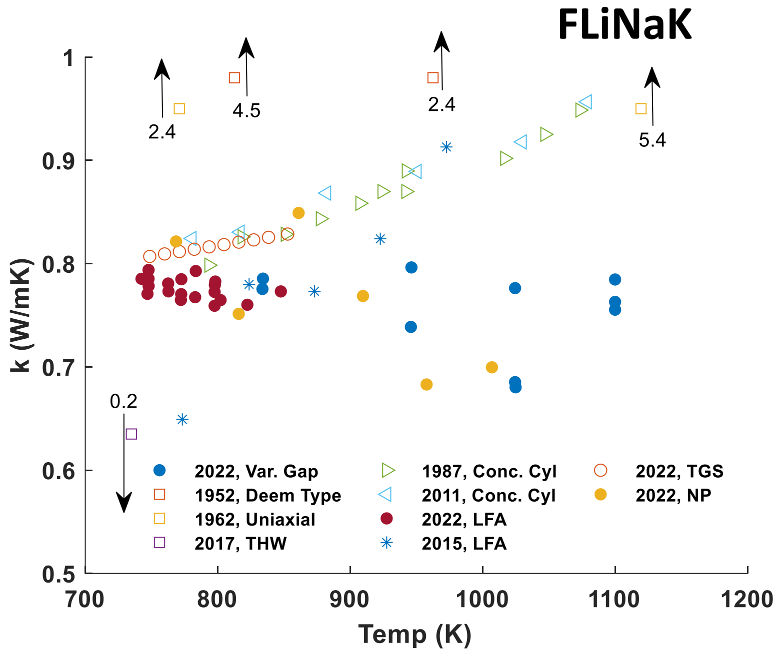
Outline

- Motivation
- Necessary conditions for thermal measurements
- Description of methods
- Results from a needle probe sensor
- Future outlook
- Summary

Motivation

Motivation – Limited data

- Large variability within the literature on measured properties
- Absence of data on multiple properties for many salt mixtures
- Thermal conductivity (k) is difficult to measure and predict
- No standard measurement approach
- Debate about expected trend of dk/dT



MSTDB-TP (2.0)

	Entries	% of F-salts	k data	% of F-salts
Total MSTDB-TP entries	488	--	25	--
Fluoride salt entries	290	100%	17	6%
Entries w/ LiF,NaF,KF,BeF$_2$,ZrF$_4$,UF$_4$	261	**90%**	14	**5%**
Entries w/ CaF$_2$,GdF$_3$,LaF$_3$,MgF$_2$, NdF$_3$,NpF$_3$,PuF$_4$,SrF$_2$,ThF$_4$,UF$_3$	29	10%	3	1%
Entries with UF$_4$	150	**52%**	5	**2%**

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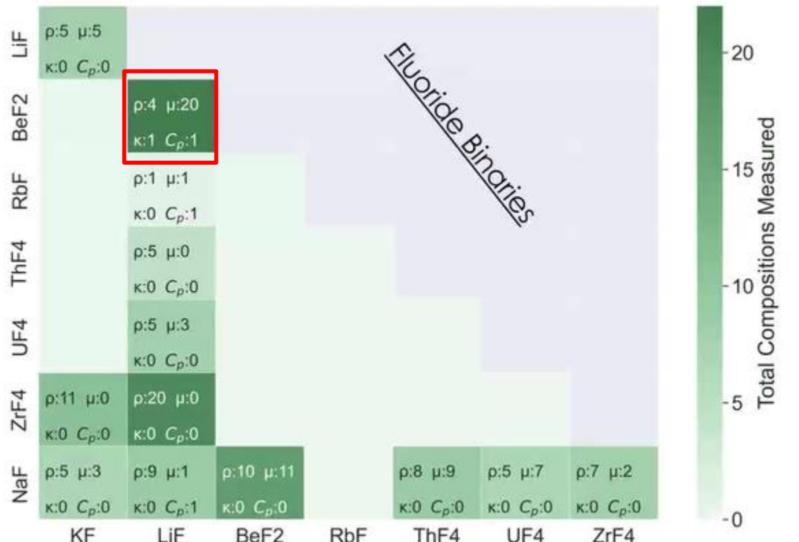
	AlCl3	KCl	NaCl	MgCl2	UCl3	LiCl	PuCl3	ThCl4
KCl	ρ:4 μ:4 κ:0 C_p:0							
NaCl	ρ:3 μ:8 κ:0 C_p:0	ρ:6 μ:6 κ:0 C_p:0						
MgCl2		ρ:13 μ:8 κ:1 C_p:1	ρ:10 μ:8 κ:0 C_p:0					
UCl3		ρ:16 μ:1 κ:0 C_p:0	ρ:8 μ:0 κ:0 C_p:0					
LiCl		ρ:5 μ:6 κ:0 C_p:1	ρ:6 μ:0 κ:0 C_p:0		ρ:10 μ:0 κ:0 C_p:0			
PuCl3			ρ:2 μ:0 κ:0 C_p:0					
ThCl4			ρ:13 μ:0 κ:0 C_p:0					
UCl4		ρ:12 μ:0 κ:0 C_p:0	ρ:8 μ:0 κ:0 C_p:0		ρ:11 μ:0 κ:0 C_p:0	ρ:14 μ:0 κ:0 C_p:0		

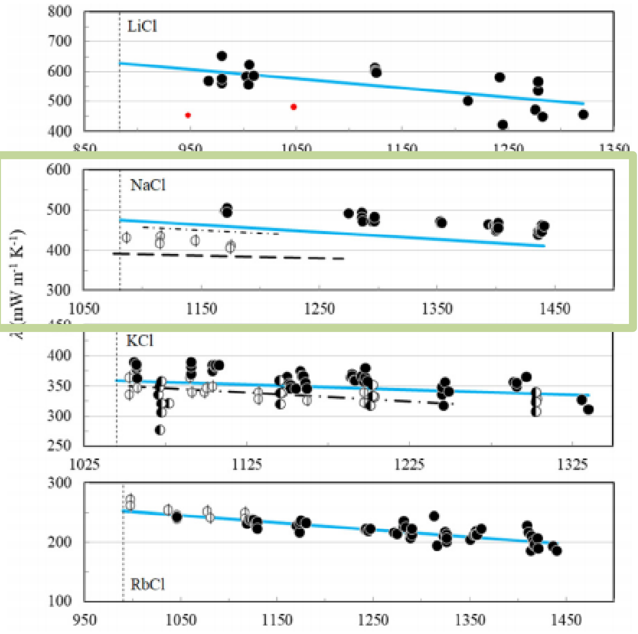


	KF	LiF	BeF2	RbF	ThF4	UF4	ZrF4
LiF	ρ:5 μ:5 κ:0 C_p:0						
BeF2		ρ:4 μ:20 κ:1 C_p:1					
RbF		ρ:1 μ:1 κ:0 C_p:1					
ThF4		ρ:5 μ:0 κ:0 C_p:0					
UF4		ρ:5 μ:3 κ:0 C_p:0					
ZrF4	ρ:11 μ:0 κ:0 C_p:0	ρ:20 μ:0 κ:0 C_p:0					
NaF	ρ:5 μ:3 κ:0 C_p:0	ρ:9 μ:1 κ:0 C_p:1	ρ:10 μ:11 κ:0 C_p:0		ρ:8 μ:9 κ:0 C_p:0	ρ:5 μ:7 κ:0 C_p:0	ρ:7 μ:2 κ:0 C_p:0

Motivation – Reliability of data for correlations

Table 1. Data sets considered for the thermal conductivity of molten nitrate salts at 0.1 MPa

First author	Publication year	Purity[a] (mass %)	Technique employed[b]	Uncertainty quoted (%)	No. of data	Temperature range (K)	Form of data[c]
			$LiNO_3$				
Previous reference correlation							
Janz[11]	1979	. . .	(Based on McDonald[22])	20	. . .	530–730	E
Primary data							
Asahina[41]	1988	. . .	Pulse-heated flat plate (TD)	4	6	536–588	D
Omotani[29]	1984	. . .	Transient hot wire (liquid probe)	3	3	531–568	T
Secondary data							
Araki[38]	1983	. . .	Parallel plates (TD)	. . .	4	539–603	D
Tye[40]	1977	99.80	Parallel plates (TD)	. . .	6	533–623	T
McDonald[22]	1970	. . .	Concentric cylinders (2.54 mm)	5	. . .	553–728	E
Gustaffson[43]	1968	Anal	Transient plane source	10	7	532–581	T
White[21]	1967	. . .	Concentric cylinders (3.18 mm)	3	. . .	553–648	E
			$NaNO_3$				
Previous reference correlation							
Nagasaka[12]	1991	. . .	(Based on Kitade[13])	5	. . .	584–662	E
Janz[11]	1979	. . .	(Based on McDonald[22])	20	. . .	590–740	E
Primary data							
Kitade[13]	1989	99.00	Transient hot wire (insulated)	3	28	583–661	T
Asahina[41]	1988	. . .	Pulse-heated flat plate (TD)	4	5	583–651	D
Tufeu[20]	1985	. . .	Concentric cylinders (0.2 mm)	4	10	593–673	T
Omotani[28]	1982	99.90	Transient hot wire (liquid probe)	3	1	587.7	T
Odawara[44]	1977	. . .	Wave-front interferometer (TD)	. . .	9	581–691	T
Secondary data							
Zhang[31]	2000	99.95	Transient hot wire (insulated)	3	3	603–664	T
Ohta[26]	1990	. . .	Laser flash (TD)	. . .	8	592–660	D
Santini[37]	1983	. . .	Parallel plates (TD)	. . .	. . .	583–651	E
Kato[38]	1977	. . .	Parallel plates (TD)	4.5	10	595–654	D
McDonald[22]	1970	. . .	Concentric cylinders (2.54 mm)	5	. . .	593–728	E
Gustafsson[42]	1968	Anal	Transient plane source	2.6	9	588–727	T
White[21]	1967	. . .	Concentric cylinders (3.18 mm)	5	5	619–692	D
Bloom[25]	1965	Anal	Concentric cylinders (0.9 mm)	5	6	602–695	T



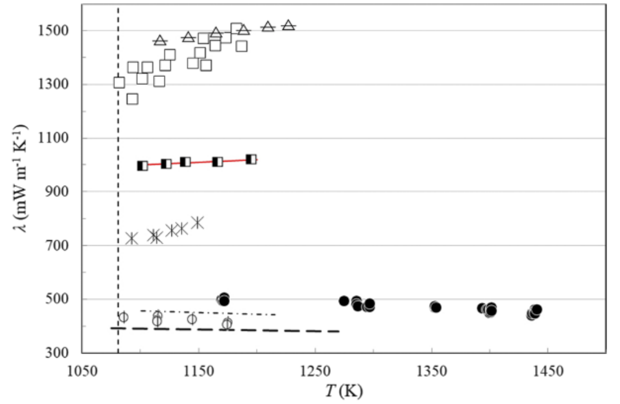


Fig. 1. Thermal conductivity at 0.1 MPa of molten NaCl as a function of the temperature. Golyshev and Gonik[3] (— —), Nagasaka *et al.*[4] (●), Smirnov *et al.*[5] (✱), Harada *et al.*[6] (Φ), Bystrai and Dessyatnik[7] (□), Veneraki *et al.*[8] (—•), Egorov and Revyakina[9] (△), Fedorov and Matsuev[10] (◧), and the reference correlation of Janz *et al.*[11] (red line); melting point temperature (- -).

Chliatzou, Ch.D., J. of Physical and Chem Ref Data, 2018

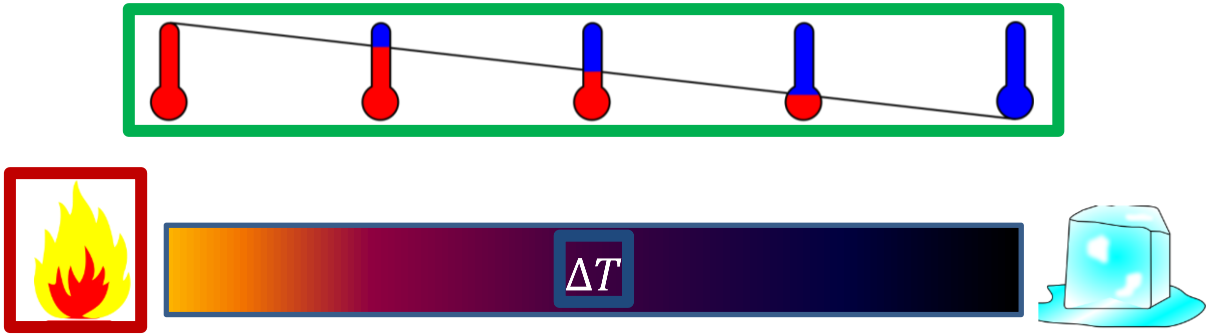
Necessary Conditions to Measure Thermal Conductivity/Diffusivity

Simplification of Measurement Process

To measure the thermal properties of a solid, the following are needed:

1. A heat source
2. A temperature change
3. An accurate temperature sensor
4. Model relating temperature and heat transfer to property

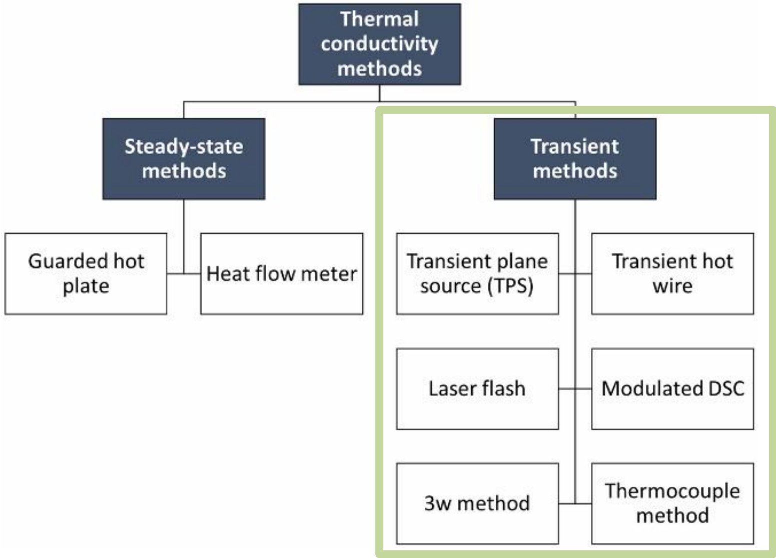
An absolute method is one where theory and experiment match so well that no calibration is needed.



$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2}$$

$$q'' = -k\frac{dT}{dx}$$

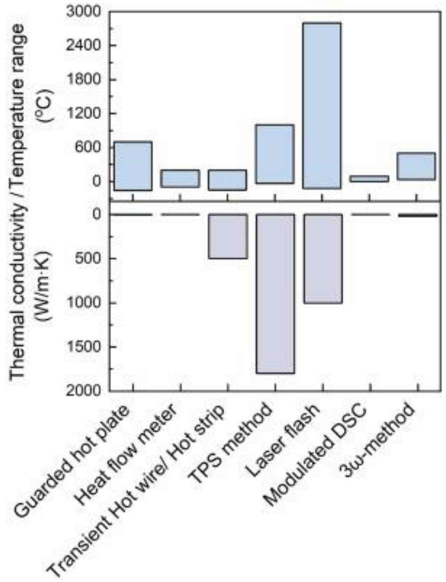
Traditional Approaches in Solids



Thermal conductivity methods

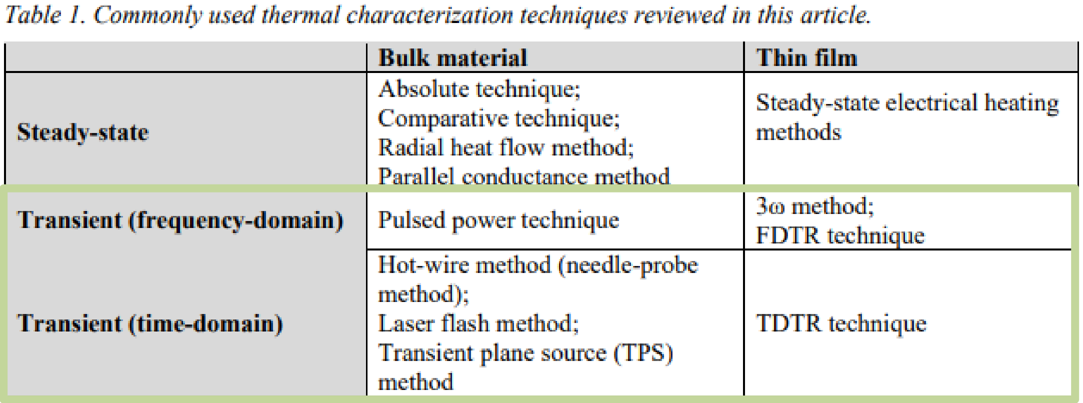
Steady-state methods
- Guarded hot plate
- Heat flow meter

Transient methods
- Transient plane source (TPS)
- Transient hot wire
- Laser flash
- Modulated DSC
- 3w method
- Thermocouple method

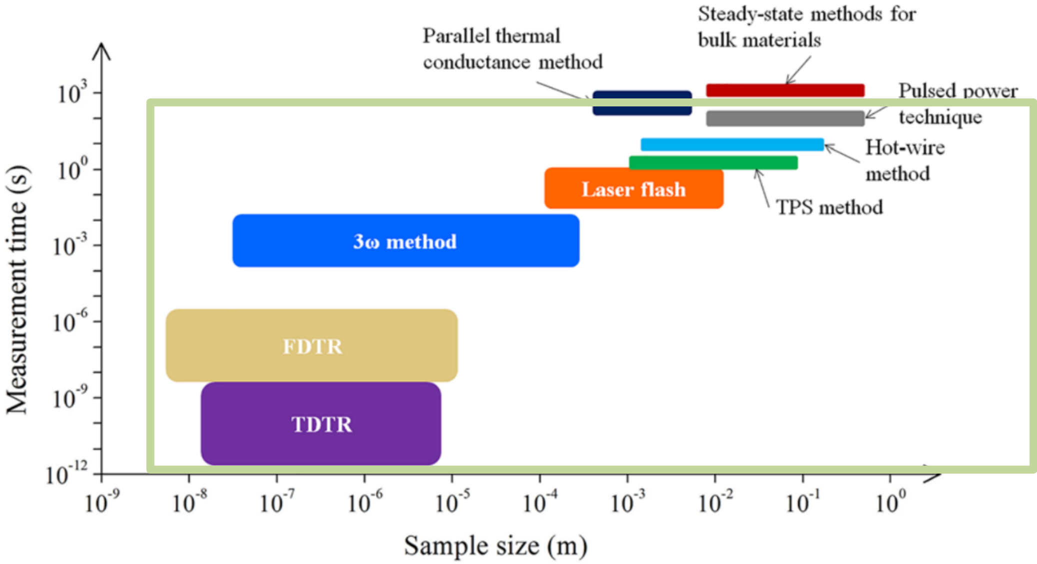


Palacios, 2019, https://doi.org/10.1016/j.rser.2019.03.020

Table 1. Commonly used thermal characterization techniques reviewed in this article.



	Bulk material	**Thin film**
Steady-state	Absolute technique; Comparative technique; Radial heat flow method; Parallel conductance method	Steady-state electrical heating methods
Transient (frequency-domain)	Pulsed power technique	3ω method; FDTR technique
Transient (time-domain)	Hot-wire method (needle-probe method); Laser flash method; Transient plane source (TPS) method	TDTR technique

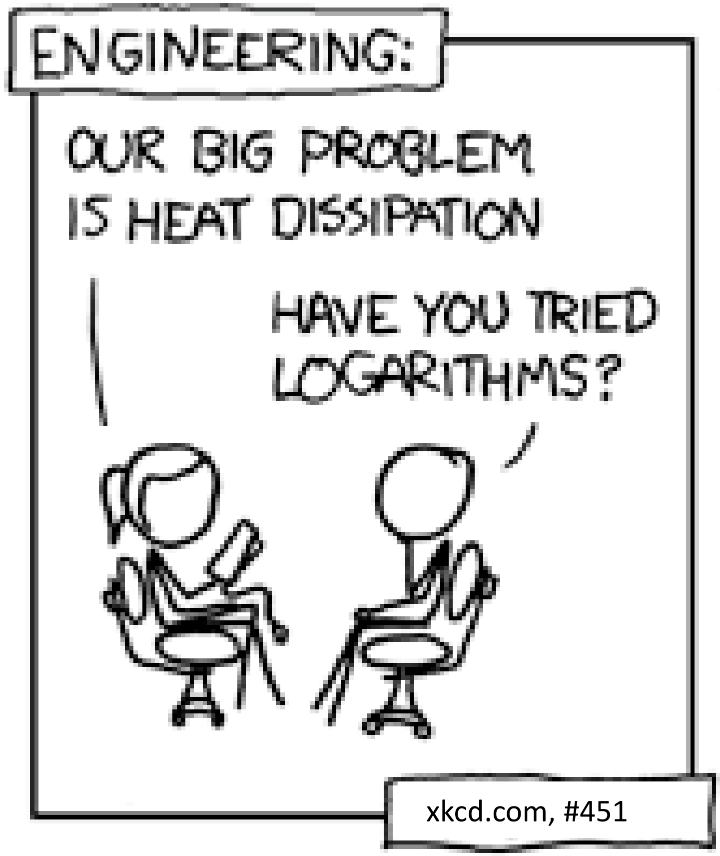


Zhao, 2016, doi: 10.1115/1.4034605

Measurement constraints not present when measuring solids

To measure molten salt thermal conductivity, the device needs to consider and deal with:

1. Electrical isolation from salt
2. Corrosion resistance
3. High temperatures
4. How to reduce convection
5. How to account for radiation
6. Sample volume
7. Measurement time
8. Glovebox compatiblity



xkcd.com, #451

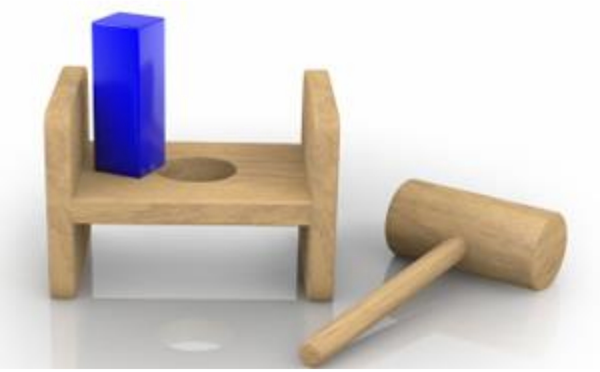
Key Problem

We are operating in a space where:

Standard techniques don’t exactly apply

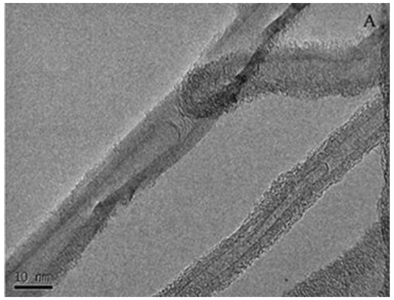
and

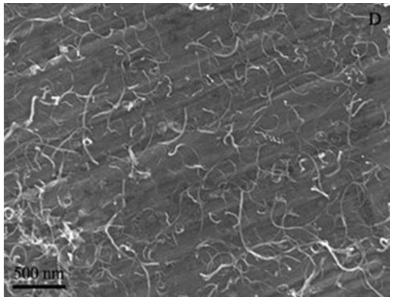
Standard reference materials don’t exist

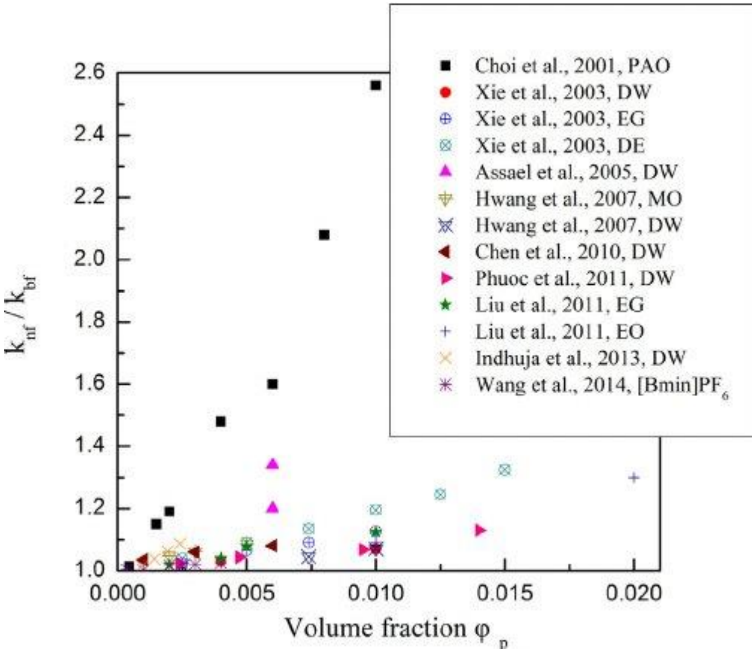


What I want us to avoid

Nanoparticle enhancement

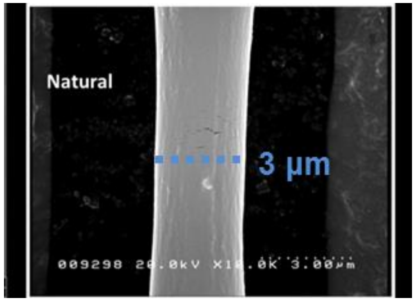


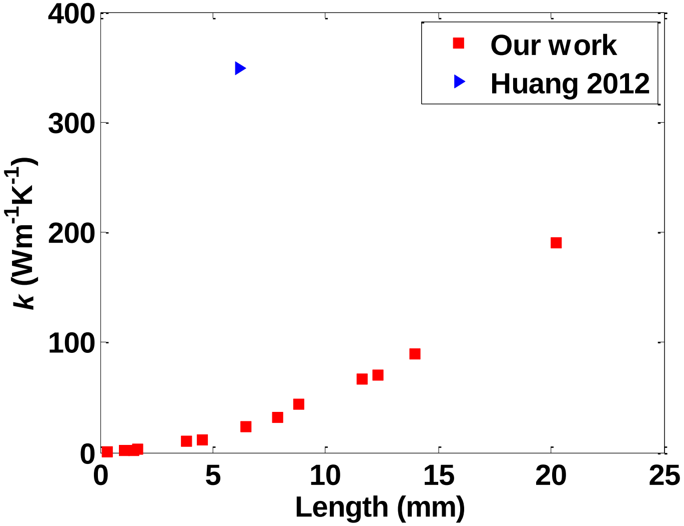




Jiang, H., 2015, DOI: 10.1016/j.jtice.2015.03.037

Spider Silk

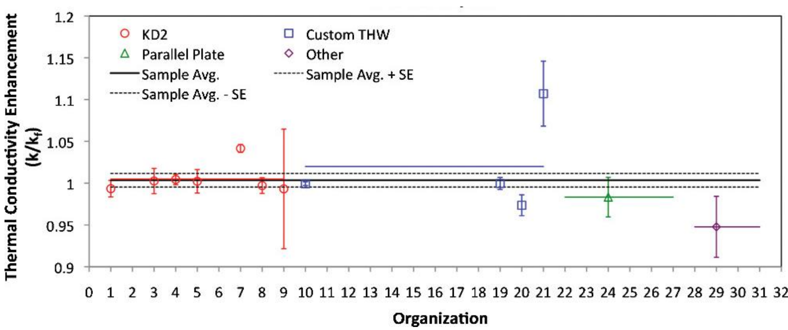




C. Xing, T. Munro, et al., *Measurement Science and Technology*, 2013.

Nano-fluids
Round-Robin testing

Organization/contact person	Experimental method[a] for thermal conductivity measurement (Ref.)
Argonne National Laboratory/E. V. Timofeeva	KD2 Pro
CEA/C. Reynaud	Steady-state coaxial cylinders[c]
Chinese University of Hong Kong/S.-Q. Zhou	Steady state parallel plate[d]
DSO National Laboratories/L. G. Kieng	Supplied nanofluid samples
ETH Zurich and IBM Research/W. Escher	THW and parallel hot plates[f]
Helmut-Schmidt University Armed Forces/ S. Kabelac	Guarded hot plate[d]
Illinois Institute of Technology/D. Venerus	Forced Rayleigh scattering[g]
Indian Institute of Technology, Kharagpur/ I. Manna	KD2 Pro
Indian Institute of Technology, Madras/T. Sundararajan, S. K. Das	THW[h]
Indira Gandhi Centre for Atomic Research/J. Philip	THW[d], KD2
Kent State University/Y. Tolmachev	KD2 Pro
Korea Aerospace University/S. P. Jang	THW[i]
Korea Univ./C. Kim	THW[d]
METSS Corp./F. Botz	THW[d]
MIT/J. Buongiorno, L.W. Hu, T. McKrell	THW[j]
MIT/G. Chen	THW[k]
Nanyang Technological University/K. C. Leong	THW[l]
NIST/M. A Kedzierski	KD2 Pro
North Carolina State University-Raleigh/J. Eapen	Contributed to data analysis
Olin College of Engineering/R. Christianson, J. Townsend	THW[n]
Queen Mary University of London/D. Wen	THW[d]
RPI/P. Keblinski	Contributed to data analysis
SASOL of North America/Y. Chang	Supplied nanofluid samples
Silesian University of Technology/A. B. Jarzebski, G. Dzido	THW[o]
South Dakota School of Mines and Technology/H. Hong	Hot Disk[p]
Stanford University/P. Gharagozloo, K. Goodson	IR thermometry[q]
Texas A&M University/J. L. Alvarado	KD2 Pro
Ulsan National Institute of Science and Technology; Tokyo Institute of Technology/I. C. Bang, J. H. Kim	KD2 Pro
Université Libre de Bruxelles, University of Naples/C. S. Iorio	Modified hot wall technique[r], Parallel plates[s]
University of Leeds/Y. Ding	KD2 and parallel hot plates[t]
University of Pittsburgh/M. K. Chyu	Unitherm™ 2022 (Guarded heat flow meter)
University of Puerto Rico-Mayaguez/J. G. Gutierrez	THW[u]



When ensuring experimental conditions matched theory, no large increase in k was observed

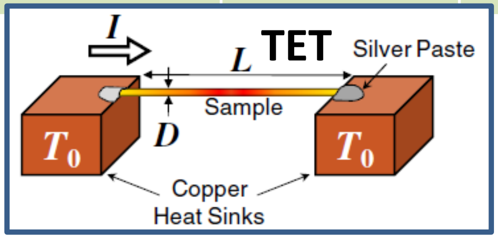
Buongiorno, Jacopo, et al. *JAP,* 2009, p. 094312.

Spider Silk

Dragline	**Reduced TET**	**Curve-Fit Red. TET**	**Full TET**	**3ω**	**Fluoro**
k (W m^{-1} K^{-1})	1.2-191 (Large error)	1.18 (25%)	1.23 (12%)	1.24 (12%)	–
α (mm^2 s^{-1})	0.65-127 (Large error)	0.63 (25%)	0.62 (12%)	0.61 (15%)	–
ρc_p (MJ m^{-3} K^{-1})	–	–	–	2.0 (15%)	–
As Spun Synth k (W m^{-1} K^{-1})	–	0.29 (25%)	0.24 (13%)	–	–
As Spun Synth α (mm^2 s^{-1})	–	0.16 (25%)	0.17 (15%)	–	–
Processed Synth α (mm^2 s^{-1})	–	0.33 (25%)	–	–	0.3 (25%)

When radiation heat loss was included to account for large surface area-to-volume ration, reasonable values of k were observed

1.2 W/m K, instead of 400 W/m K



Description of Methods

Optical, electrical heating

Thermal Conductivity/Diffusivity Techniques

- Parallel plate method
  - Variable gap
- Concentric cylinders
- Forced Rayleigh scattering
  - Transient grating spectroscopy (TGS)
- Transient hot-wire (THW)
  - Needle probe
  - 3ω
- Laser flash (LFA)
- Modulated photothermal radiometry (MPR)
- Time domain thermoreflectance (TDTR)

Institution	**Approach for α, k, e**
ORNL	Variable gap apparatus (k)
ANL	LFA (α)
INL	LFA (α)
PNNL	LFA (α)
LANL	LFA (α)
CNL	LFA (α)
JRC	LFA (α)
Univ. of Ariz./ Georgia Tech	LFA (α)
Ural Rus. Aca. Sci.	LFA (α)
Huazhong U. Sci. Tech.	LFA (α)
NCSU	TDTR (k)
UCSD	3ω (k), MPR (e)
MIT	TGS (α)
Univ. Rome	Needle probe (k*)
BYU	THW (k), Needle Probe (k)

*max 200 °C

Variable Gap Apparatus
(variant of heat flow meter)

The Variable-Gap Technique for Measuring Thermal Conductivity of Fluid Specimens

J.W. COOKE

Operation

- Using heaters with known output and heat sinks, establish a temperature difference across a thin layer of the sample ($L < 300\ \mu m$)
- Record the temperatures along the centerline above and below sample after reaching steady state
- Repeat at different thicknesses and analyzing using Fourier’s law, $k = (\Delta L/\Delta T) * q"$

Drawbacks

- Steady state can still result in convective heat losses (based on gap thickness)
- Requires careful design to minimize radial heat losses
- Requires calibration since heat flux is hard to directly measure

$$\Delta T_s = (Q/A)\Delta x_s/k_s$$

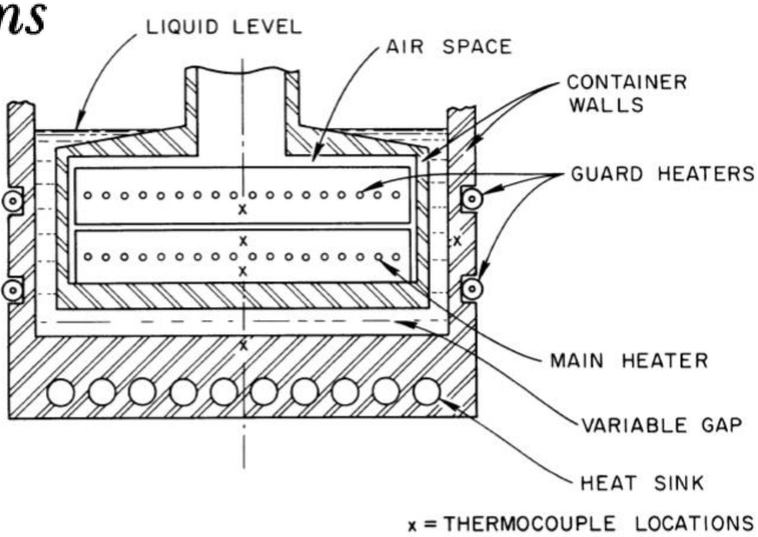
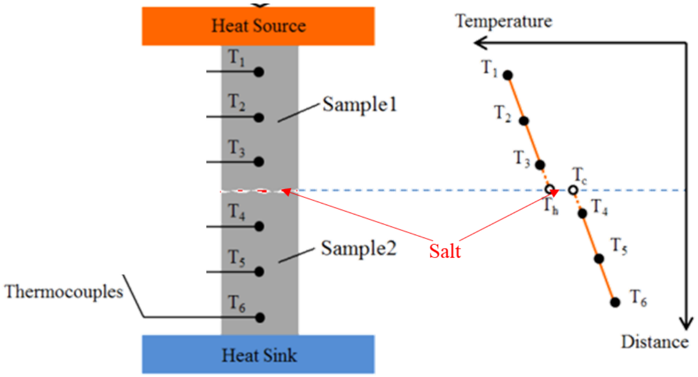
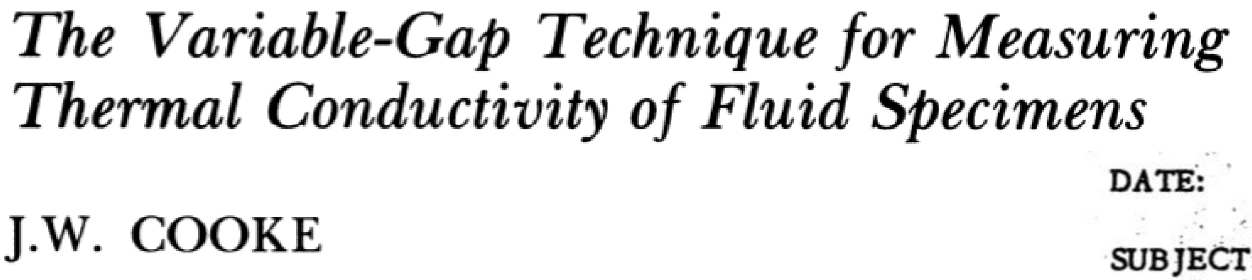


FIGURE 1. Schematic drawing of a variable-gap thermal conductivity cell.



Zhao, Dongliang,et al. *Journal of Electronic Packaging*, 2016.

Variable Gap Apparatus
(variant of heat flow meter)



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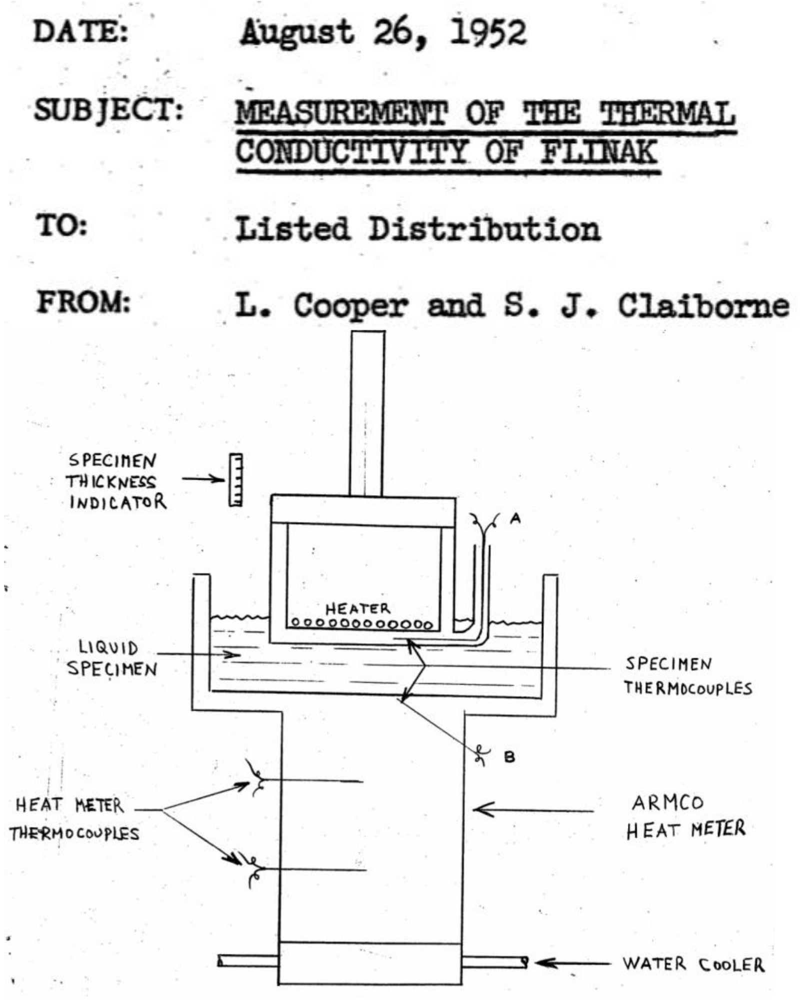


DATE: August 26, 1952

SUBJECT: MEASUREMENT OF THE THERMAL CONDUCTIVITY OF FLINAK

TO: Listed Distribution

FROM: L. Cooper and S. J. Claiborne

Concentric Cylinders

Heat capacity and thermal conductivity of molten ternary lithium, sodium, potassium, and zirconium fluorides mixtures

V. Khokhlov *, I. Korzun, V. Dokutovich, E. Filatov

Journal of Nuclear Materials 410 (2011) 32–38

Operation

- Create gap between cylinders of low emissivity material
- Using heaters with known output and heat sinks, establish a temperature difference across a thin ring of the sample
- Record the temperatures across the gaps after reaching steady state
- Fit using $k = (\Delta L/\Delta T) * q$“, and considers radiation

Drawbacks

- Steady state can still result in convective heat losses
- Difficult the ensure uniform gap
- Requires careful design to minimize axial heat losses
- Requires calibration since heat flux is hard to directly measure

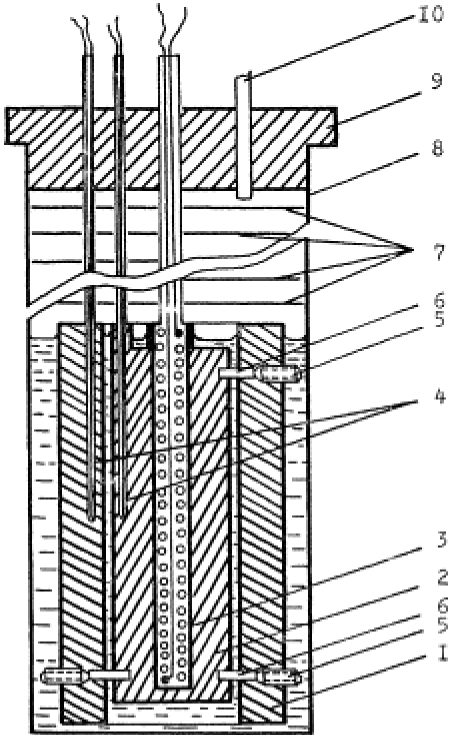
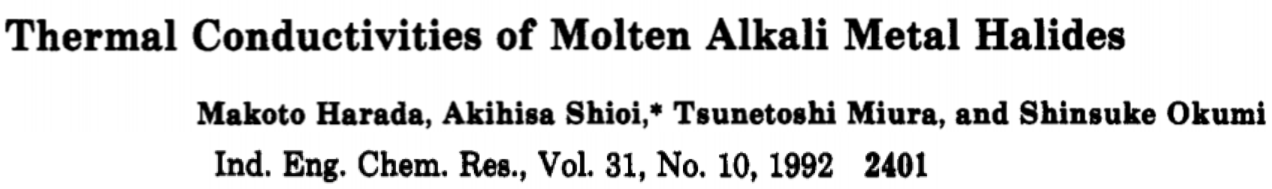


Fig. 1. Device for measuring the thermal conductivity: 1, external cylinder; 2, internal cylinder; 3, heater; 4, thermocouples; 5, fixing screws; 6, thermal shields; 7, thermal screens; 8, cooled tube; 9, rubber stopper; 10, pipe for evacuation and supply of inert gas.

Laser Flash



Thermal Conductivities of Molten Alkali Metal Halides

Makoto Harada, Akihisa Shioi,* Tsunetoshi Miura, and Shinsuke Okumi

Ind. Eng. Chem. Res., Vol. 31, No. 10, 1992 **2401**

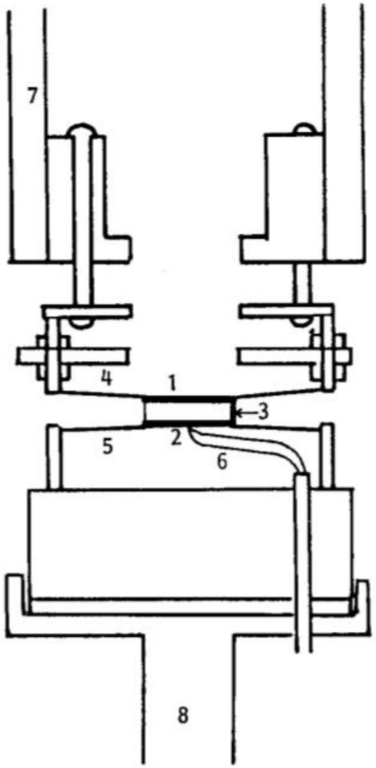


Figure 2. Detailed description of measuring device for LF-II: 1, platinum disk (upper); 2, platinum disk (lower); 3, quartz chips; 4 and 5, platinum wire; 6, Pt–Pt/13% Rh thermocouple; 7, upper rod; 8, support rod.

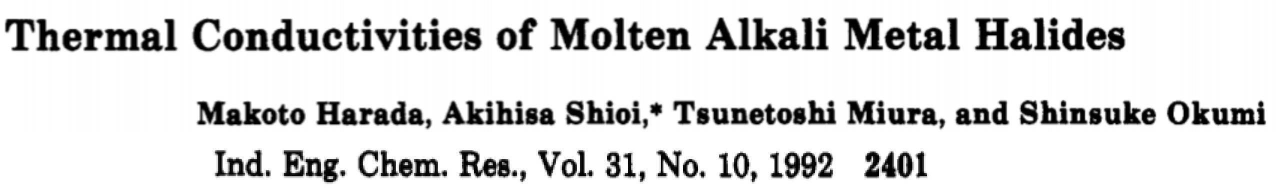
Operation

- Laser pulse into sample (or crucible)
- Resulting temperature rise on opposite side measured
- α determined by half time to maximum intensity

Drawbacks

- Requires a 3-layer model to determine α
- To determine k from α, also need ρ and c_p
- Careful consideration is needed to eliminate convection or parasitic heat losses
- Relative method

Laser Flash



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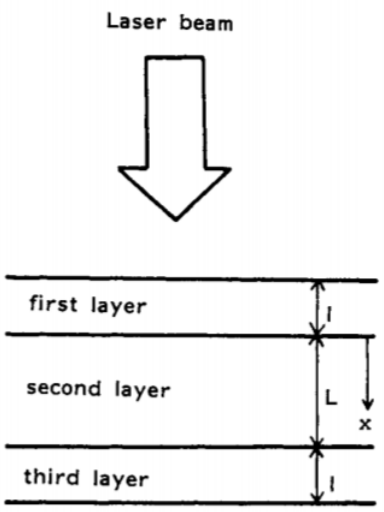
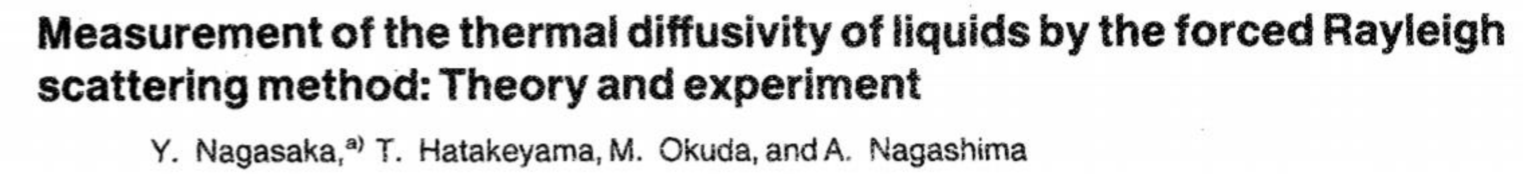


Forced Rayleigh Scattering/ Transient Grating Spectroscopy (TGS)



Measurement of the thermal diffusivity of liquids by the forced Rayleigh scattering method: Theory and experiment

Y. Nagasaka,[a] T. Hatakeyama, M. Okuda, and A. Nagashima

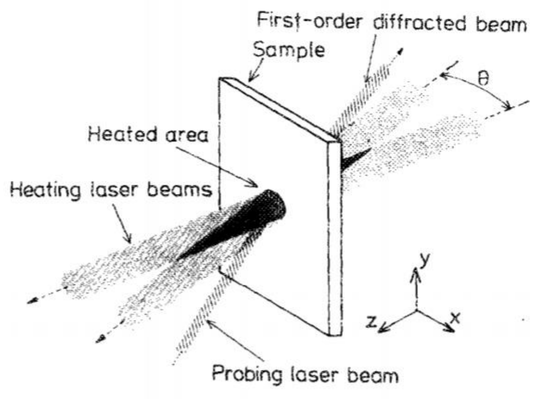
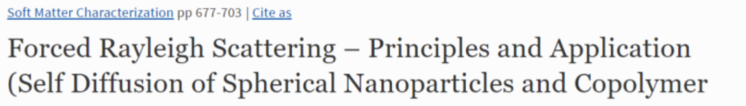


FIG. 1. Principle of the forced Rayleigh scattering method.

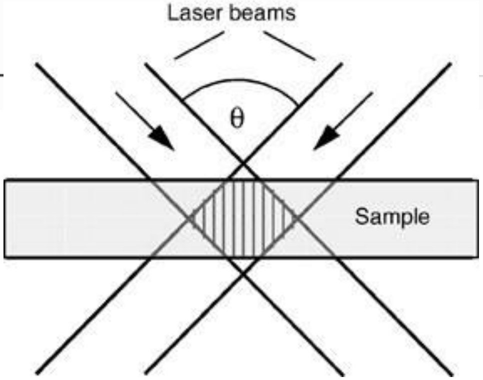


Soft Matter Characterization pp 677-703 | Cite as

Forced Rayleigh Scattering – Principles and Application (Self Diffusion of Spherical Nanoparticles and Copolymer Micelles)

Authors

W. Schärtl



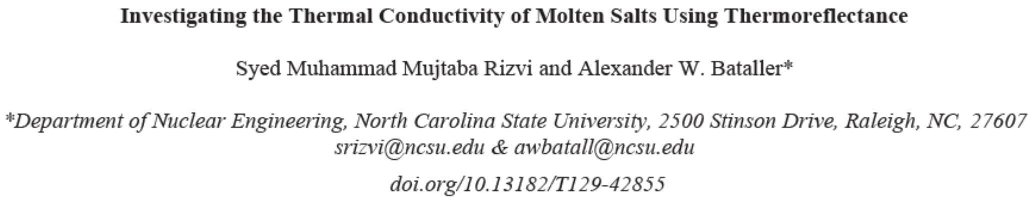
Operation

- An interference pattern is created by splitting and then crossing modulated laser beams
- A probe beam is diffracted as function of time as the interference pattern stretches and shrinks
- α is determined from the spacing of the grating and change in intensity of the probe as function of time

Drawbacks

- Highly dependent on absorption and transmission bands of the liquid (or added dopants)
- To determine k from α, also need ρ and c_p
- Sample size can impact the heat transfer model
- Optical access to salt is required (issues with window clouding)

Time Domain Thermoreflectance (TDTR)



Investigating the Thermal Conductivity of Molten Salts Using Thermoreflectance

Syed Muhammad Mujtaba Rizvi and Alexander W. Bataller*

**Department of Nuclear Engineering, North Carolina State University, 2500 Stinson Drive, Raleigh, NC, 27607*
srizvi@ncsu.edu & awbatall@ncsu.edu

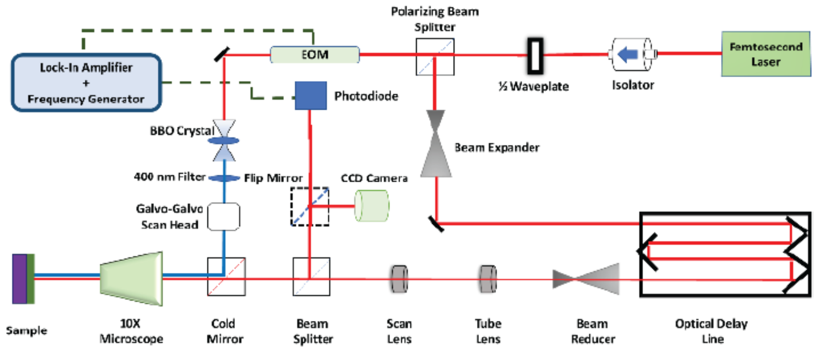
doi.org/10.13182/T129-42855

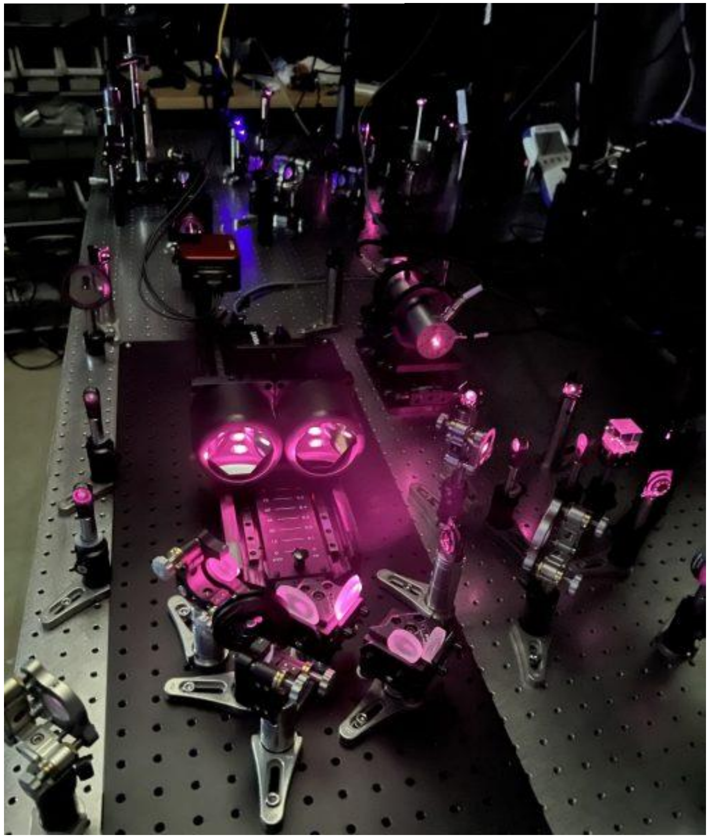
Operation

- Salt is deposited onto a substrate with a thin metallic (often gold) film
- Pulsed lasers heat the surface and the temperature-dependent change in reflectance of the film is captured with a modulated probe beam
- The delay between lasers is changed and the phase delay is fit to determine properties

Drawbacks

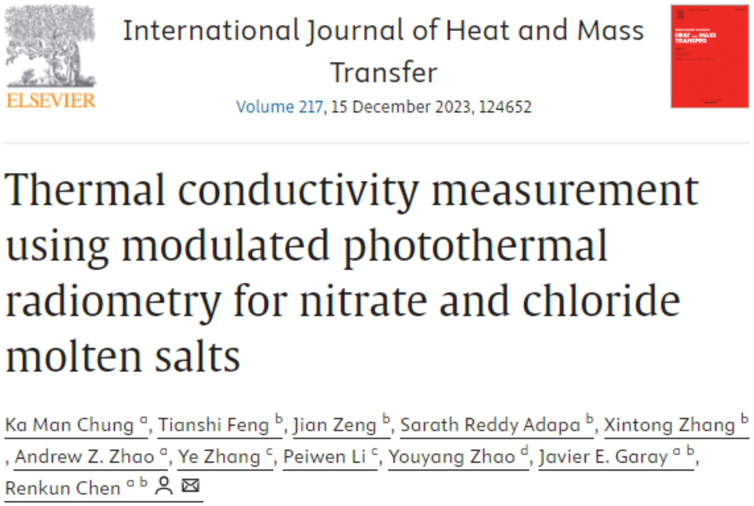
- Costly instrumentation
- Material compatibility issues
- Optical access to salt is required





https://ne.ncsu.edu/ufsg/research/

Modulated Photothermal Radiometry (MPR)



ELSEVIER

International Journal of Heat and Mass Transfer

Volume 217, 15 December 2023, 124652

Thermal conductivity measurement using modulated photothermal radiometry for nitrate and chloride molten salts

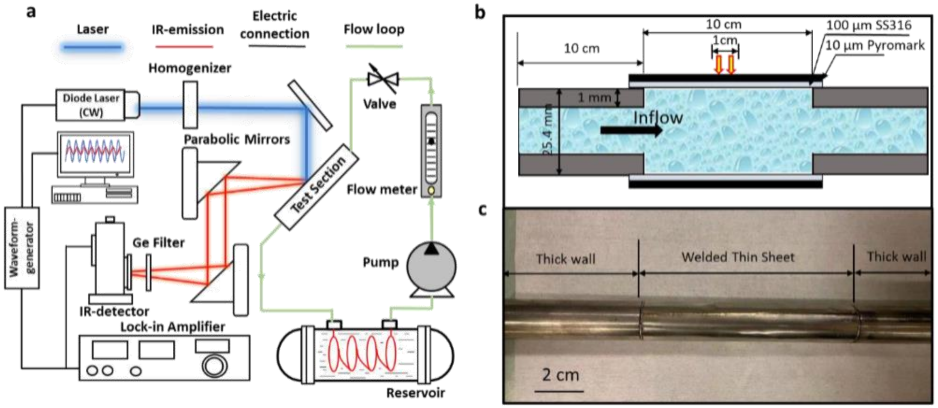
Ka Man Chung [a], Tianshi Feng [b], Jian Zeng [b], Sarath Reddy Adapa [b], Xintong Zhang [b], Andrew Z. Zhao [a], Ye Zhang [c], Peiwen Li [c], Youyang Zhao [d], Javier E. Garay [a b], Renkun Chen [a b]

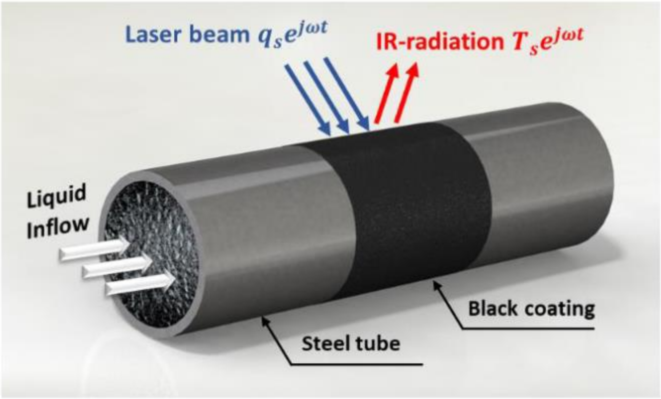
Operation

- Coatings are applied on the outside (black laser absorption and IR emission) and inside (Pt for corrosion protection) of an Inconel sheet welded onto a tube
- Modulated laser light heats the sheet and IR light is collected
- Thermal effusivity, $e = \sqrt{k\rho c_p}$ is determined by the amplitude of the IR light compared to the modulation frequency

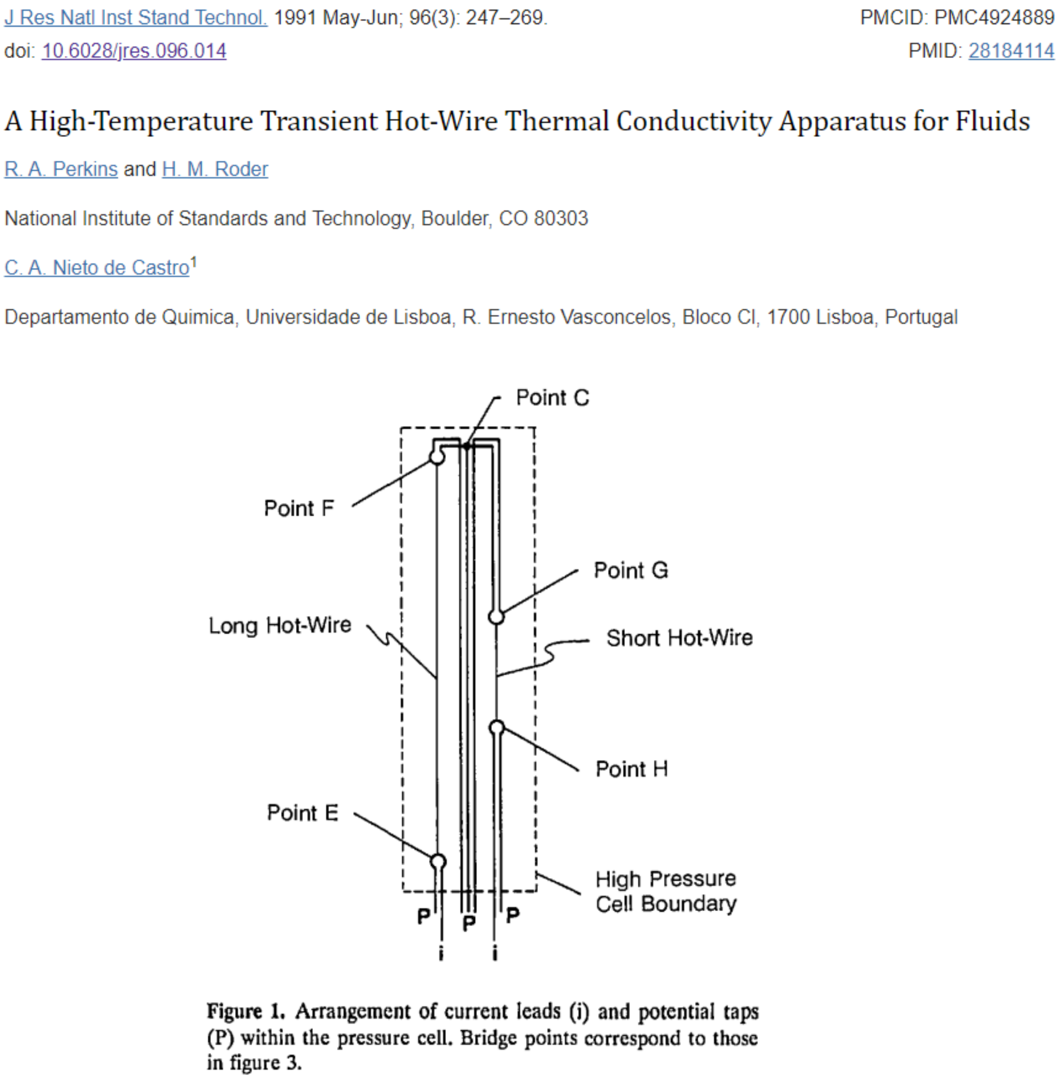
Drawbacks

- Requires calibration
- $e = \sqrt{k\rho c_p}$ is measured, requiring ρc_p to calculate k
- Requires larger amounts of salt





Transient Hot Wire



J Res Natl Inst Stand Technol. 1991 May-Jun; 96(3): 247–269.
doi: 10.6028/jres.096.014

PMCID: PMC4924889
PMID: 28184114

A High-Temperature Transient Hot-Wire Thermal Conductivity Apparatus for Fluids

R. A. Perkins and H. M. Roder

National Institute of Standards and Technology, Boulder, CO 80303

C. A. Nieto de Castro[1]

Departamento de Quimica, Universidade de Lisboa, R. Ernesto Vasconcelos, Bloco Cl, 1700 Lisboa, Portugal

Figure 1. Arrangement of current leads (i) and potential taps (P) within the pressure cell. Bridge points correspond to those in figure 3.

Operation (with salts)

- Power is supplied to a thin, glass tube filled with mercury
- The resistance and temperature of the mercury is measured

Standard operation in elec. conductive fluids

- Power is supplied to a thin, centimeter long, oxidized tantalum wire
- The wire is split between a long and a short section to remove edge effects
- A series of corrections is applied to the wire temperature to account for non-ideal effects
- Termed “absolute method” requiring no calibration, and extensive theoretical background to determine k
- Gold standard identified by former IUPAC committee

Drawbacks

- Requires electrical isolation between “wire” and salt
- Temperatures limited by materials (oxide on tantalum wire up to 400 °C)

3ω

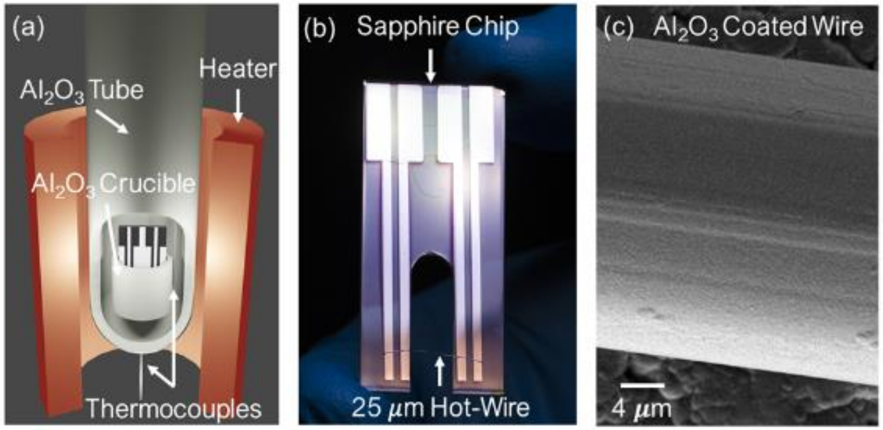
Journal of Chemical&Engineering Data

Frequency-Domain Hot-Wire Measurements of Molten Nitrate Salt Thermal Conductivity

Andrew Z. Zhao, Matthew C. Wingert, and Javier E. Garay*

Cite this: *J. Chem. Eng. Data* 2021, 66, 1, 262–270
Publication Date: December 7, 2020
https://doi.org/10.1021/acs.jced.0c00621

Article Views	Altmetric	Citations
496	1	13

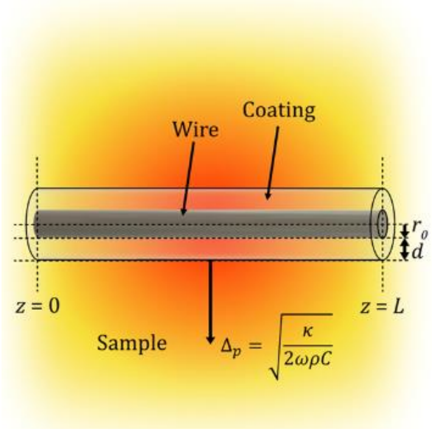


Operation (with salts)

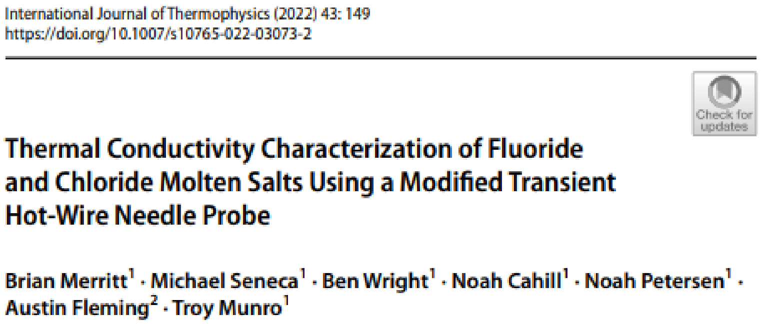
- Modulated current (1ω) is supplied to a thin, alumina coated platinum wire
- The voltage at the 3rd harmonic (3ω) is measured as a function of frequency
- Thermal model is fit to in- and out-of-phase temperature to determine k

Drawbacks

- Current materials incompatible with fluoride salts
- Temperatures limited by coating/wire bonding during thermal expansion



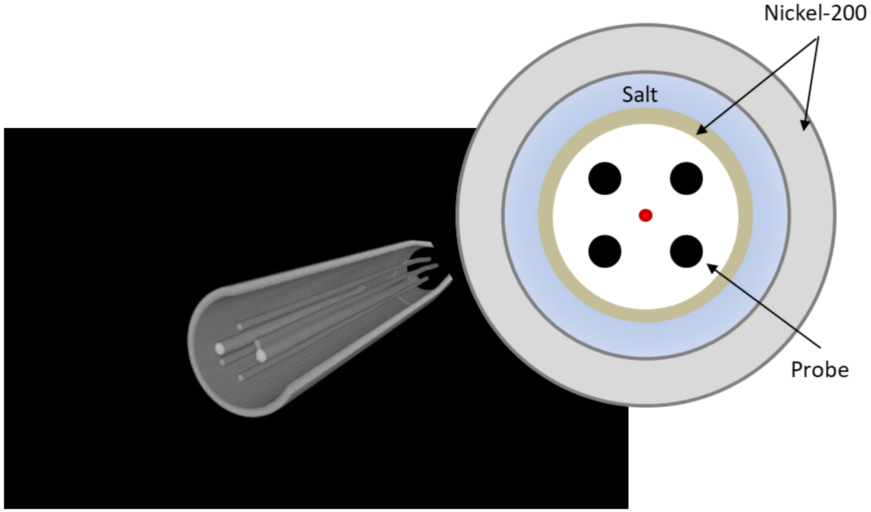
Needle Probe – Modified Transient Hot Wire, combined with Concentric Cylinders



International Journal of Thermophysics (2022) 43: 149
https://doi.org/10.1007/s10765-022-03073-2

Thermal Conductivity Characterization of Fluoride and Chloride Molten Salts Using a Modified Transient Hot-Wire Needle Probe

Brian Merritt[1] · Michael Seneca[1] · Ben Wright[1] · Noah Cahill[1] · Noah Petersen[1] · Austin Fleming[2] · Troy Munro[1]



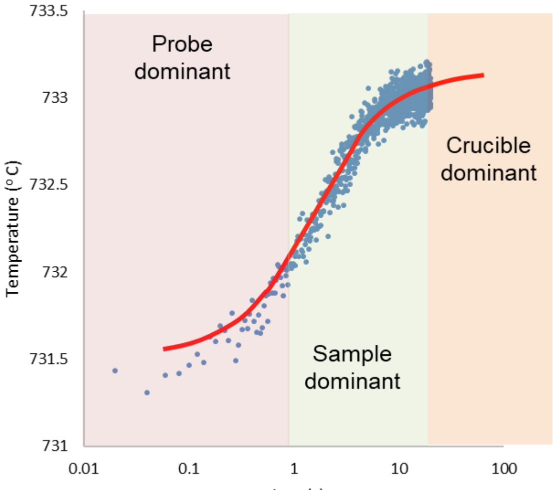
Corradini, M., 2017, NEUP Report, Advanced instrumentation for transient reactor testing

Operation

- A thin annulus of salt (~300 μm thick) is melted between the probe and surrounding crucible
- Heat is applied to a thin wire within the probe, while a thermocouple measures the centerline temperature
- k is calculated by fitting the transient temperature rise to a 3 layer thermal model

Drawbacks

- Most sensitive to probe-crucible concentricity
- Temperature limit of 750 °C
- Deviates from theory at short times due to lumping probe properties

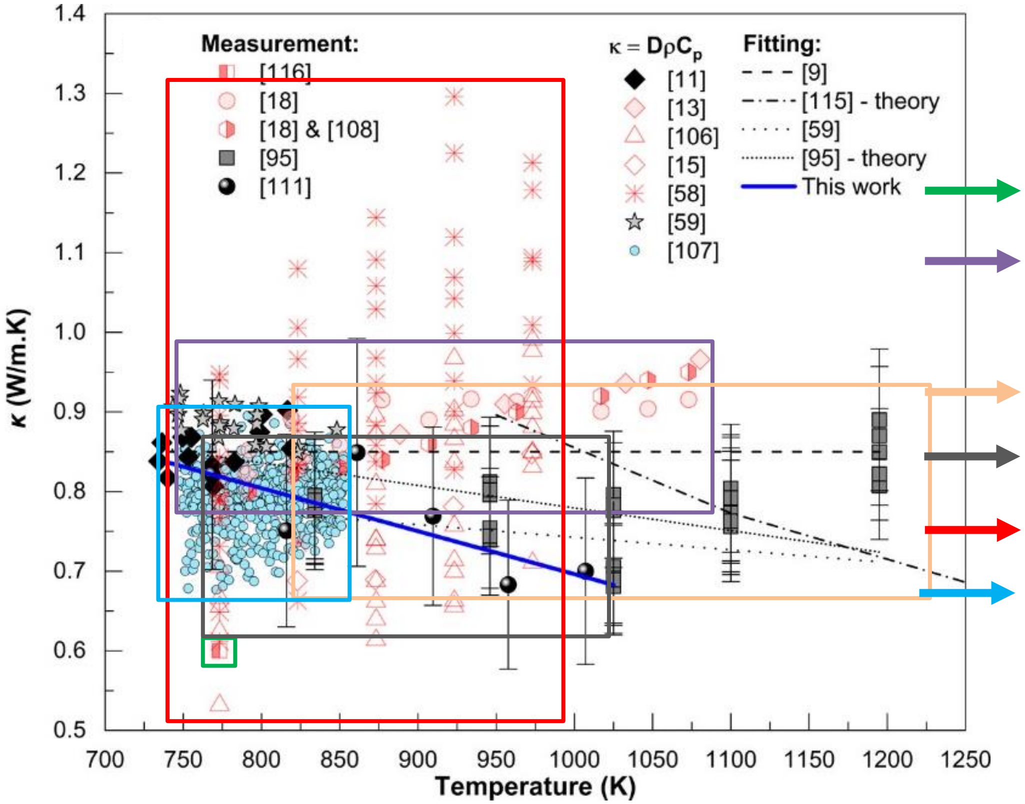


Summary of Approaches

Technique	Properties
Concentric cylinders	Main: k
Variable gap	Main: k
LFA	Main: $\alpha = k\rho^{-1}c_p^{-1}$
TGS/Rayleigh scattering	Main: $\alpha = k\rho^{-1}c_p^{-1}$
TDTR	Main: k, Secondary: ρc_p
Modulated photothermal radiometry	Main: $e = \sqrt{\rho c_p k}$
Transient hot wire	Main: k, Secondary: ρc_p
3ω	Main: k, Secondary: ρc_p
Needle probe	Main: k, Secondary: ρc_p

Summary of Approaches

**LiF-NaF-KF (FLiNaK)
measurements by method**



Uncoated Transient hot wire – Ueki [116] ◧

Concentric cylinders – Khokhlov [13]; ◇ Filatov [18]; ○

Smirnov [108]; ◐

Variable gap – Gallagher [95]; ■

Needle probe – Merritt [111]; ●

LFA – An [106]; △ Yin [15]; ◇ Rose [58]; ✳ Rudenko [59]; ☆

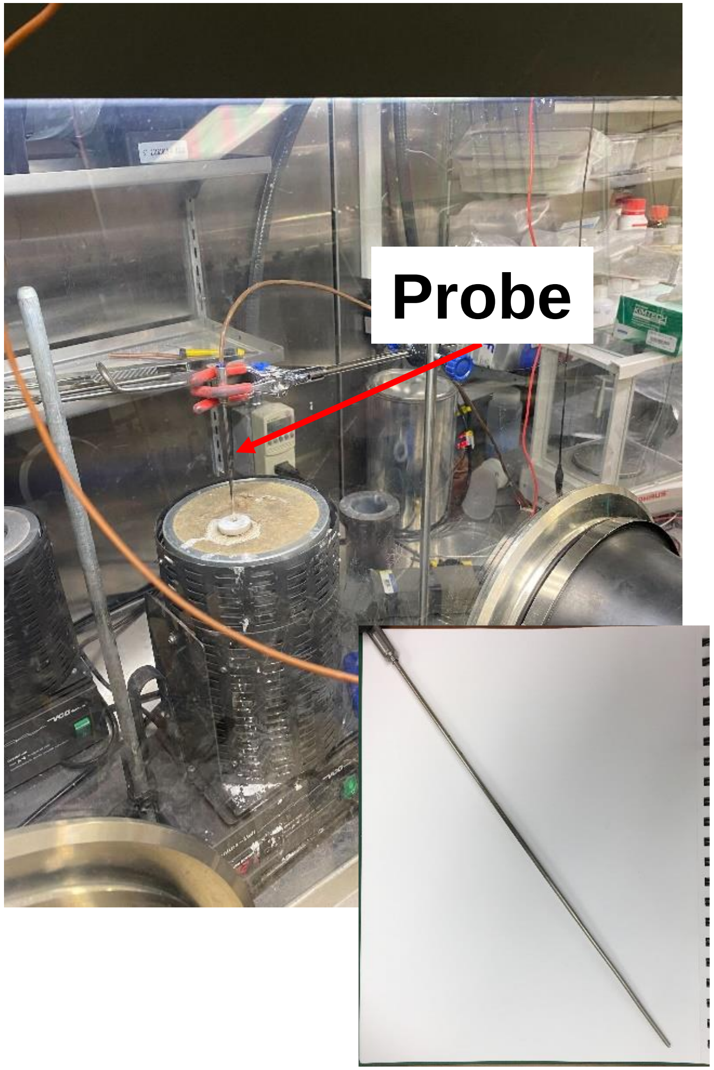
TGS/Rayleigh scattering – Robertson [107]; ●

Schorne-Pinto, J., Aziziha, M., Tisdale, H. B., Mofrad, A. M., Birri, A., Christian, M. S., ... & Besmann, T. M. (2024). Thermal Property Modeling and Assessment of the Physical Properties of FLiNaK. *ACS Applied Energy Materials*, *7*(9), 4016-4029.

What We Are Doing

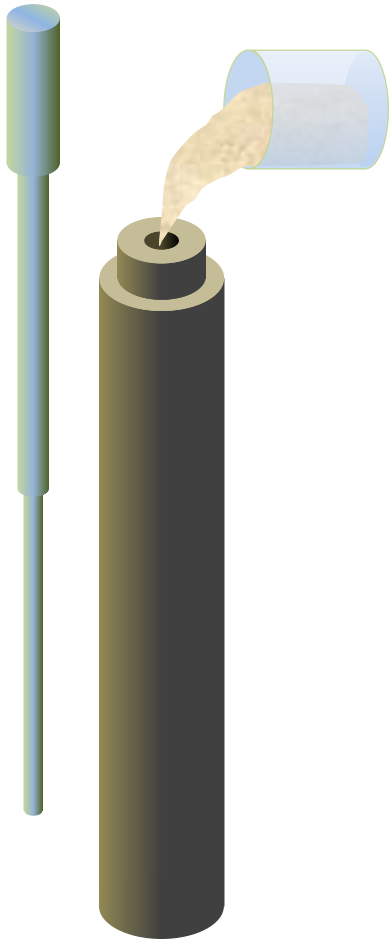
Method – Needle Probe

- Modification of the transient hot wire method (ASTM D7896-19)
  - the ASTM standard technique was used to quantify water as a standard reference liquid
  - new thermal model and uncertainty analysis is needed
- To limit convection, we combine two measurement methods:
  - the modified transient hot wire (the needle probe itself)
  - a concentric cylinders device (the crucible)

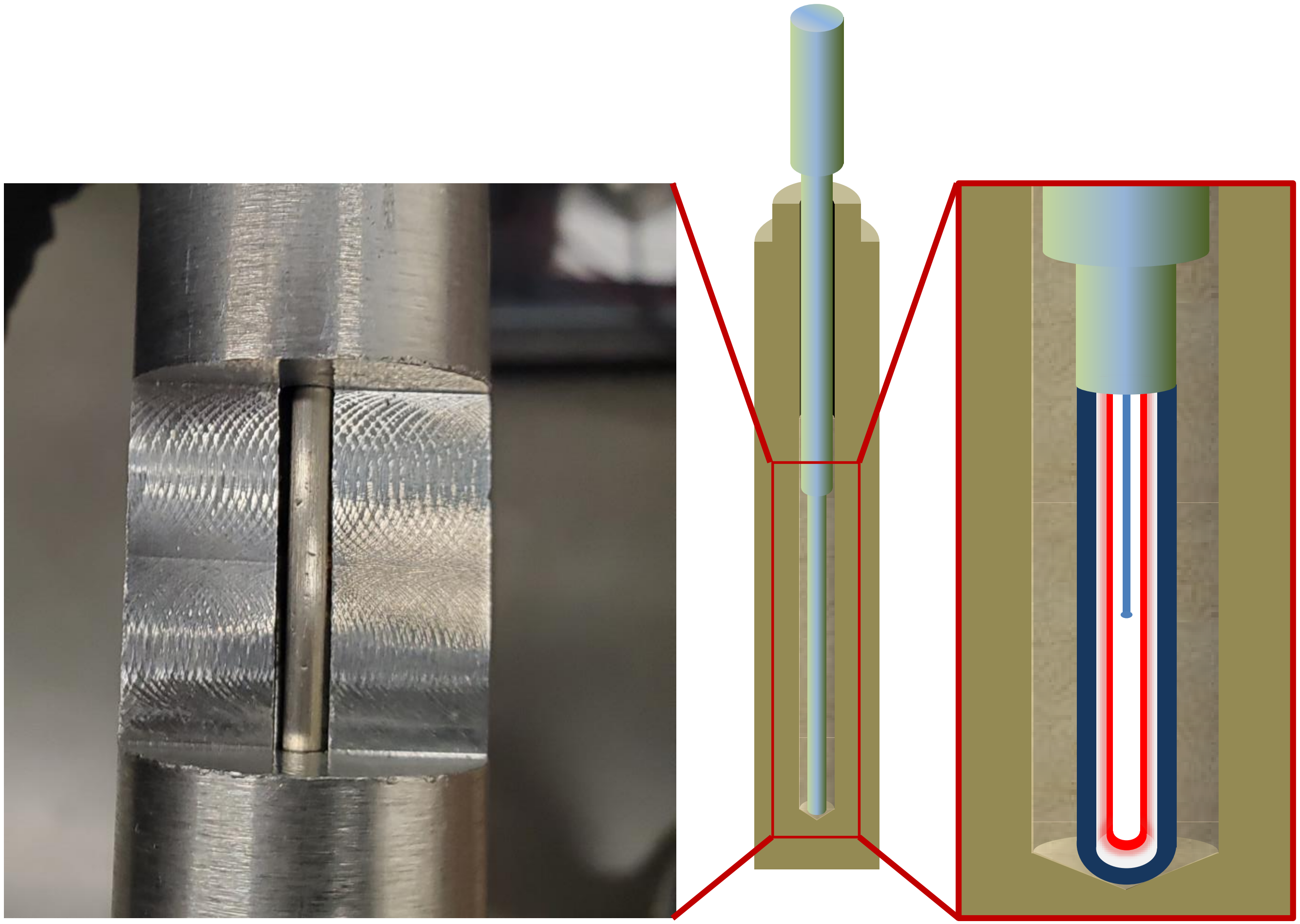


Testing Process

1. Prepare salt composition for measurement

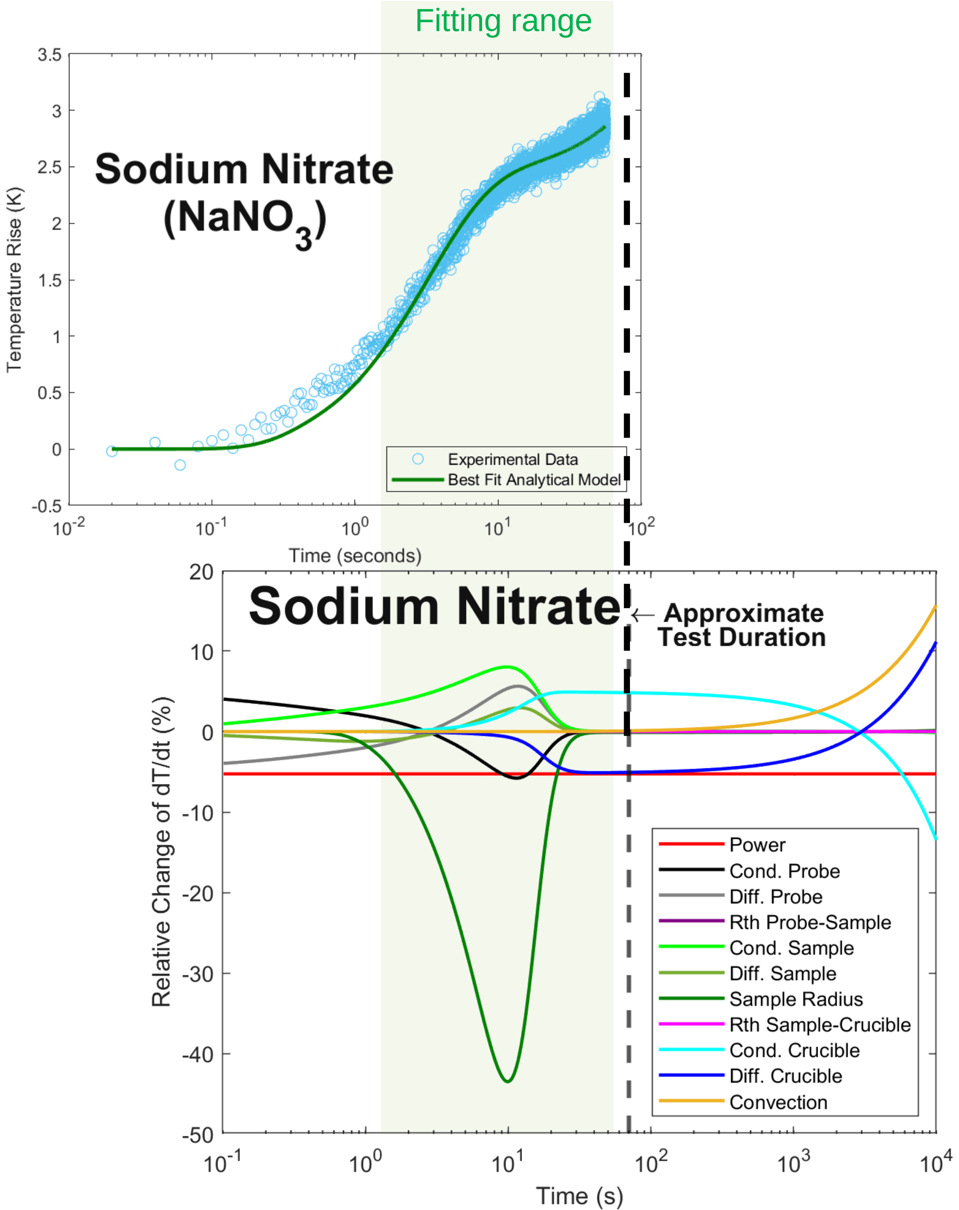


2. Electrically insulated thermocouple measures transient response to Joule heating in heater wire



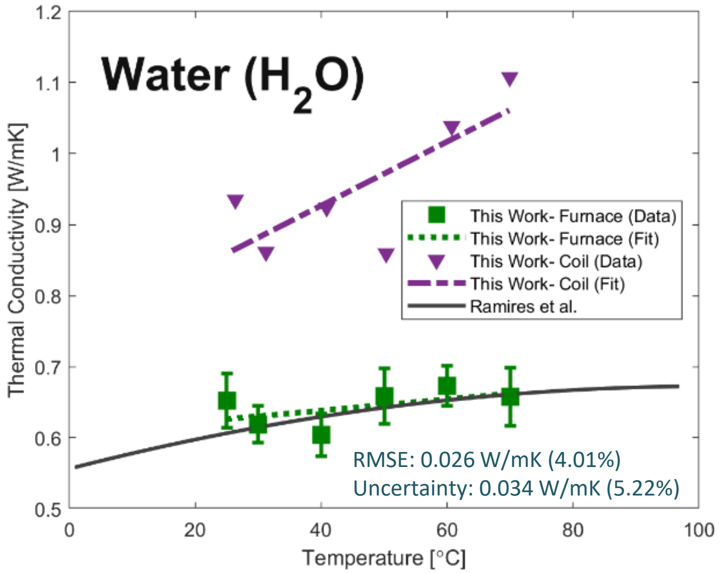
Method – Fitting to experiment

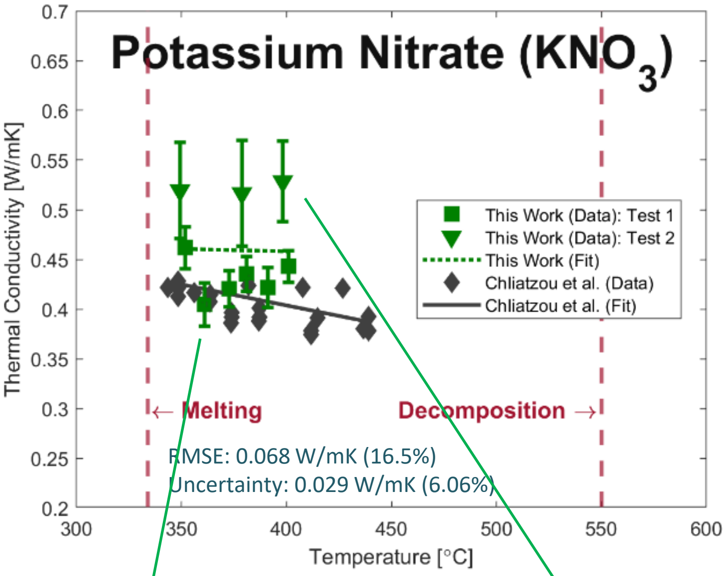
- Fitting is performed over most sensitive range for k_{sample}
- Most sensitive parameter is thickness of the salt gap, followed by salt thermal conductivity
- We don't see convection on the outside of the crucible

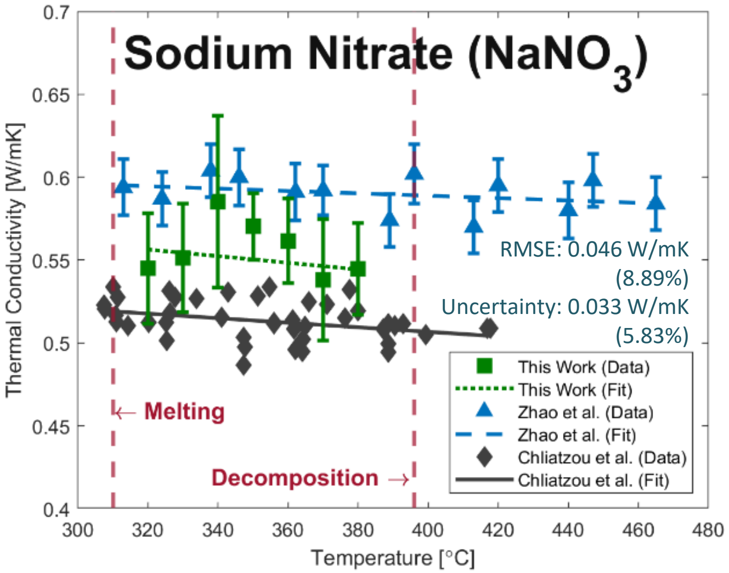


Merritt, B., et al., *Int. J. of Heat and Mass Transfer*, 189, 2022.

Results – Water and Nitrate Salts



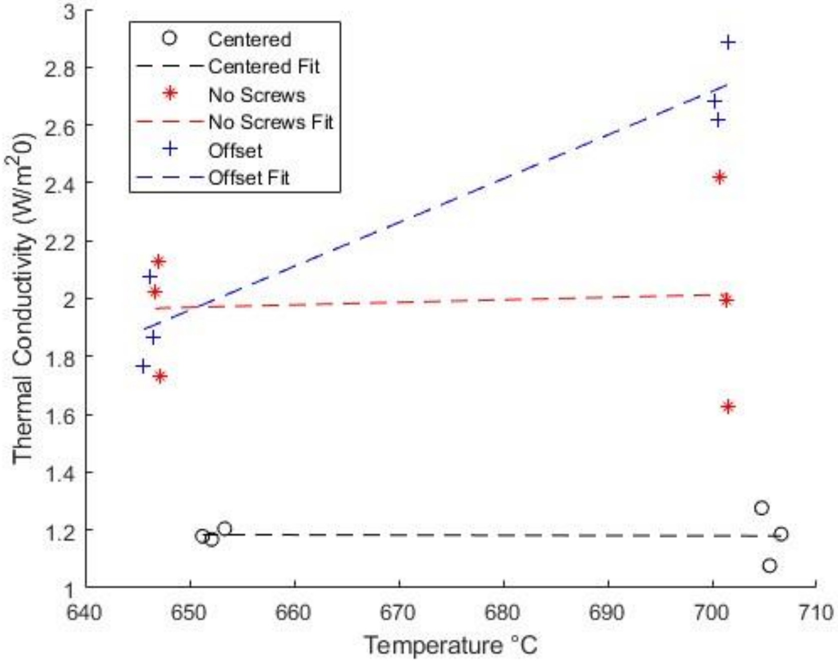




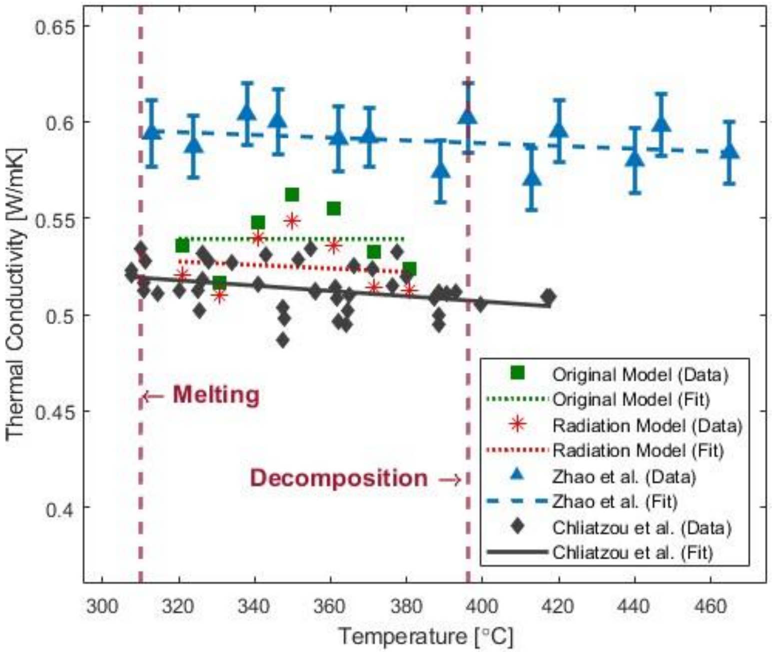
Merritt, B., et al., *Int. J. of Heat and Mass Transfer*, 189, 2022.

Impact of Model Parameters

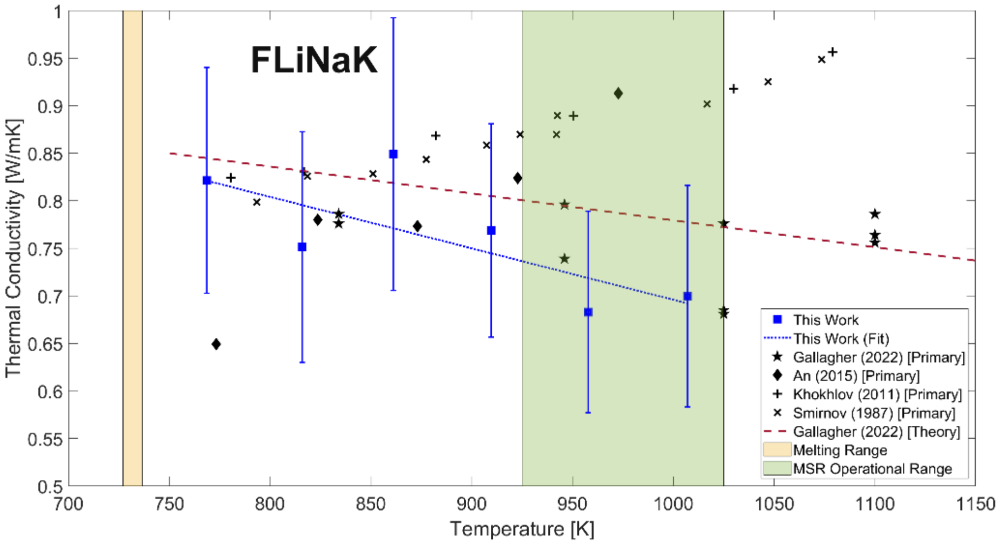
Concentricity of Probe

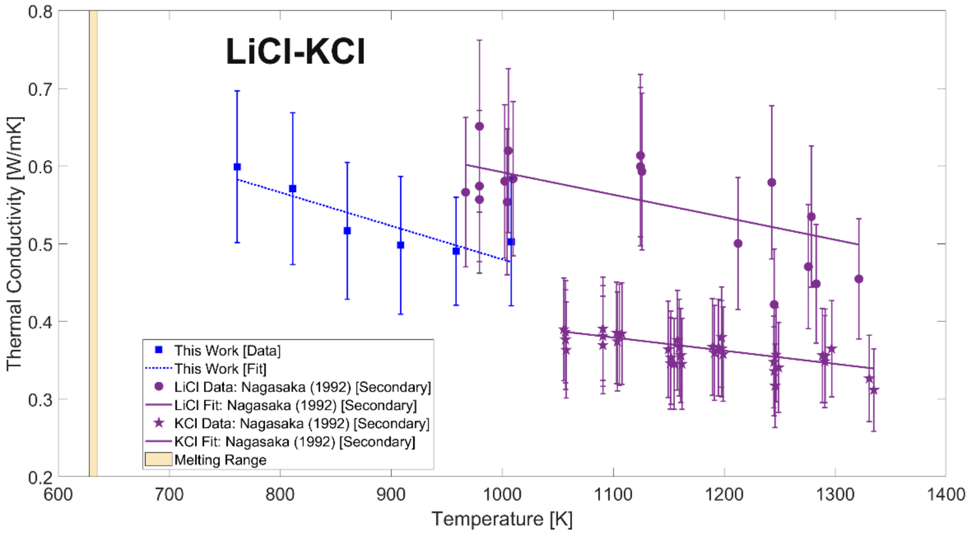


Radiation Heat Loss



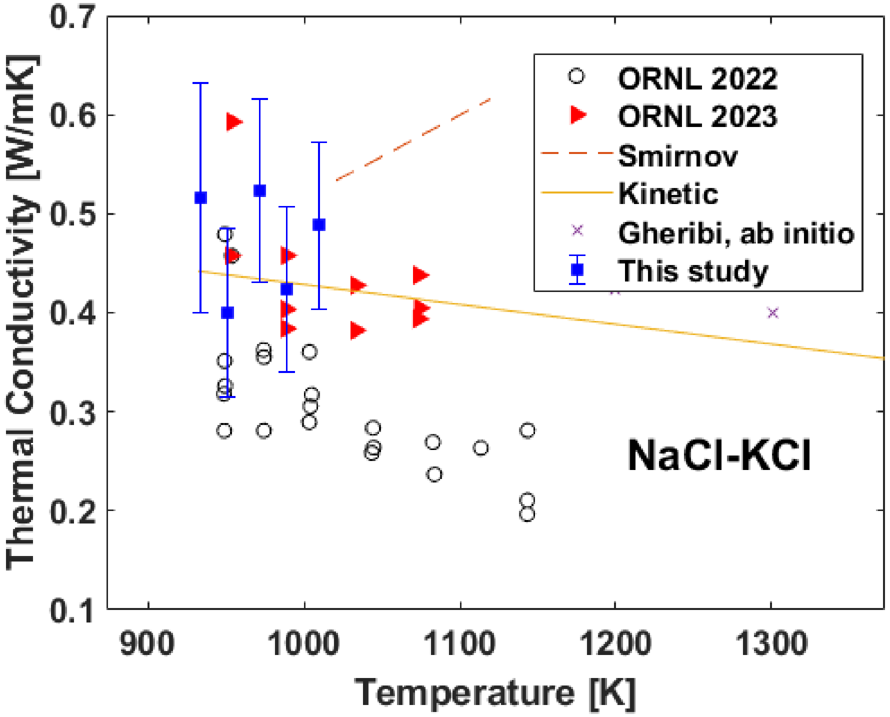
Fluoride and Chloride Salts

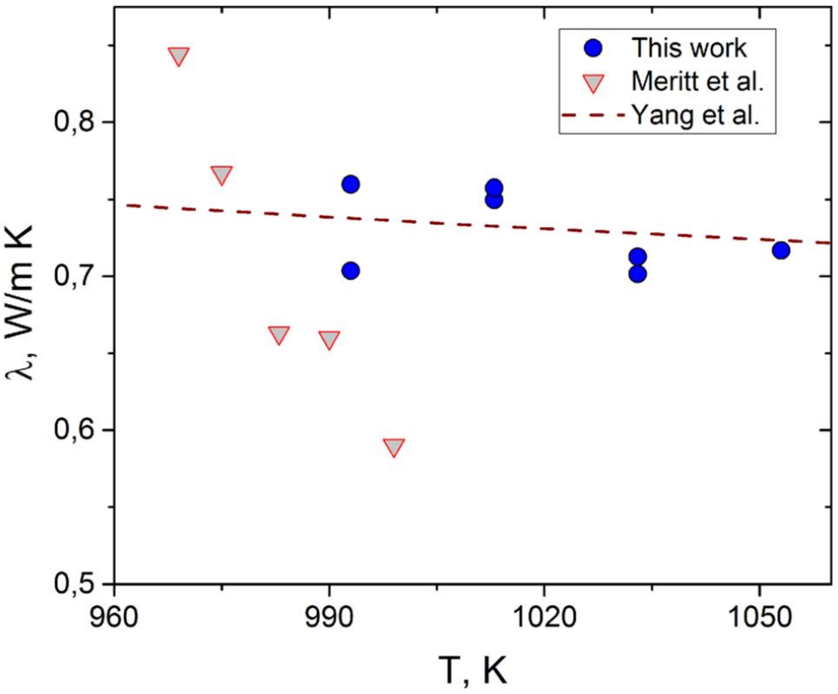




Merritt, B., et al., *Int. J. of Thermophysics*, 149, 2022.

Comparisons: Variable Gap @ ORNL LFA @ Russian Academia of Sciences, Ural



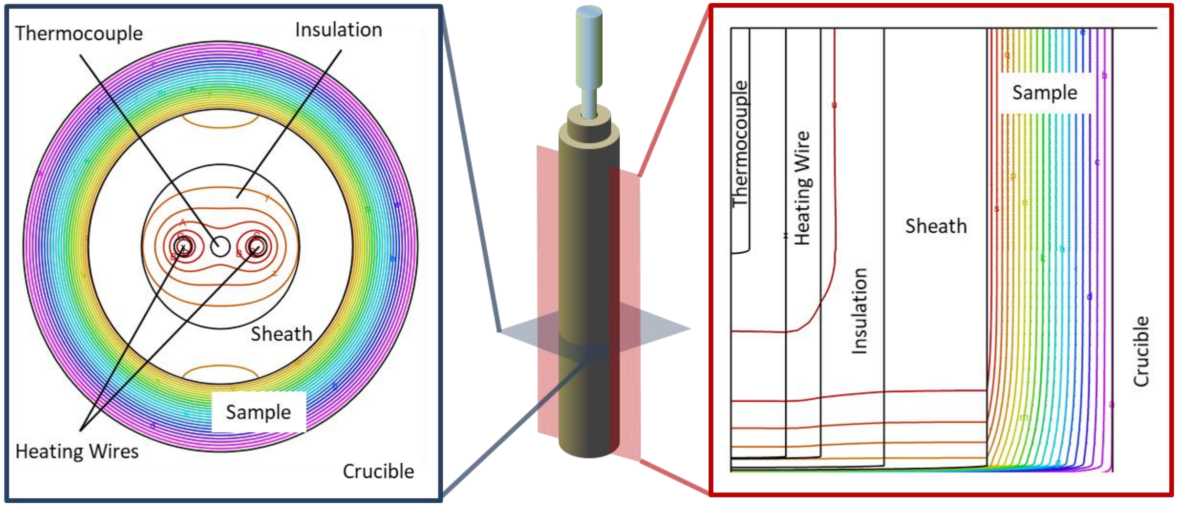


Rudenko, A., et al., *Int. J. of Thermophysics*, 45, 2024.

Needle Probe - Limitations

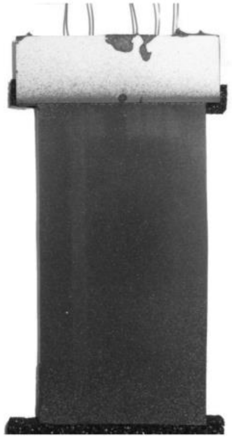
- Modeling
  - Have bi-directional heat transfer (axial and radial)
  - Multi-layer system with lumped properties
  - Analytical model requires accurate system geometry and properties
- Experiment
  - Repeated use can cause probe deformation, cracked alumina, changes to lumped thermal properties
  - Purity of sample (salt deposition can be difficult to remove)
  - Highly sensitivity to concentricity of probe
  - Temperature limit of 1023 K (750 °C)
    - Alumina electrical conductivity increases at high temperatures
    - Nickel sheath yield strength limit

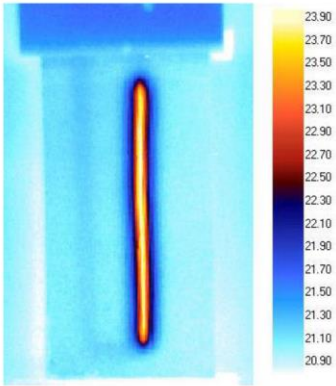
Isotherms

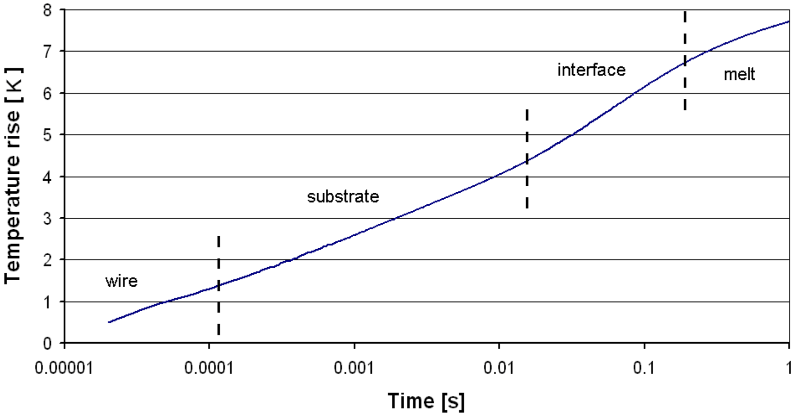


Future Outlook

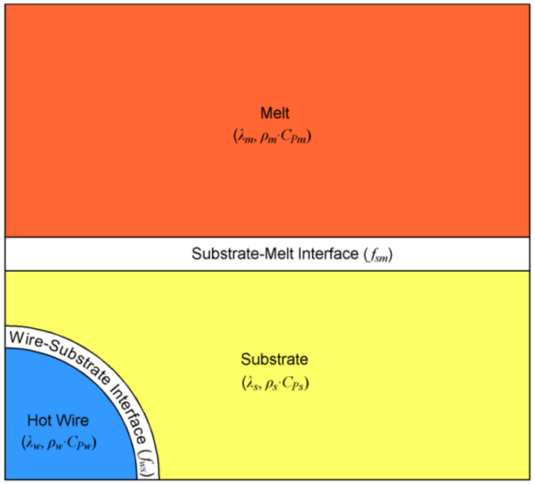
Encapsulated Transient Hot Wire (THW)

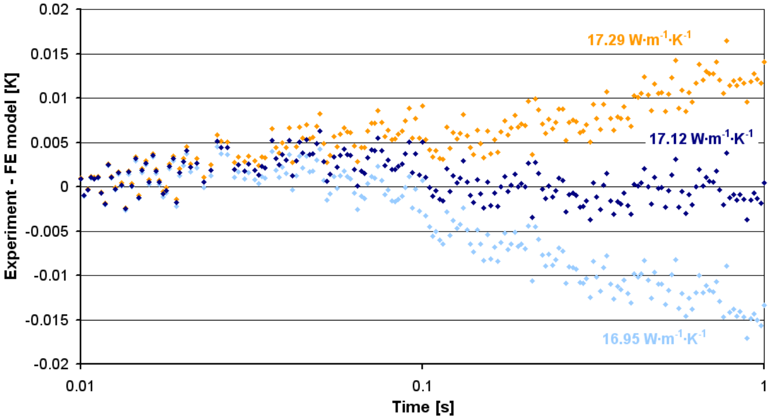






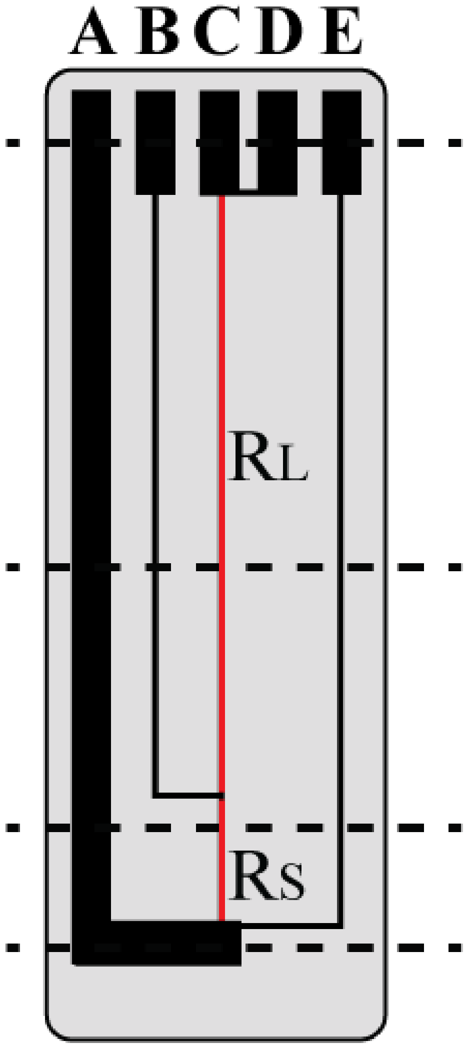
FE model

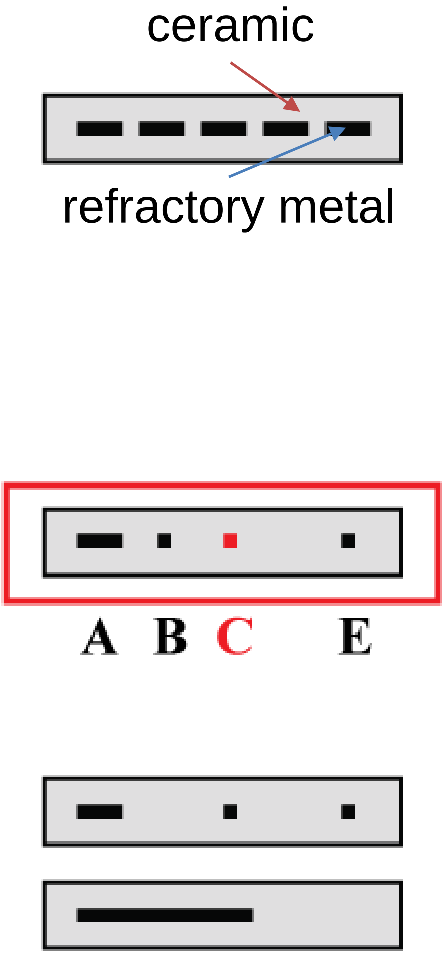


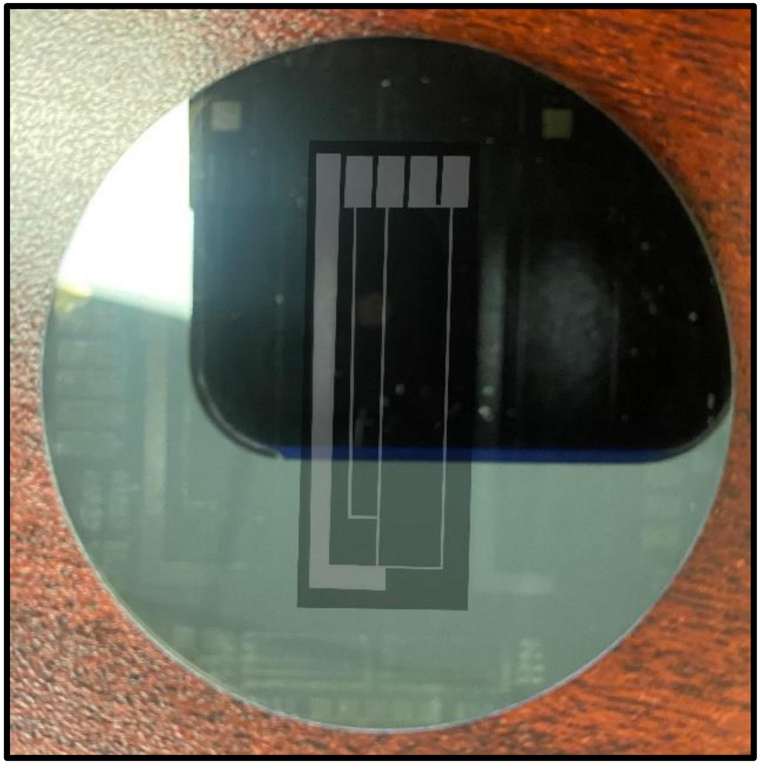


Jaromir Bilek, "Sensors for Thermal Conductivity at High Temperatures," PhD Dissertation, University of Southampton, 2006.

Initial Prototype



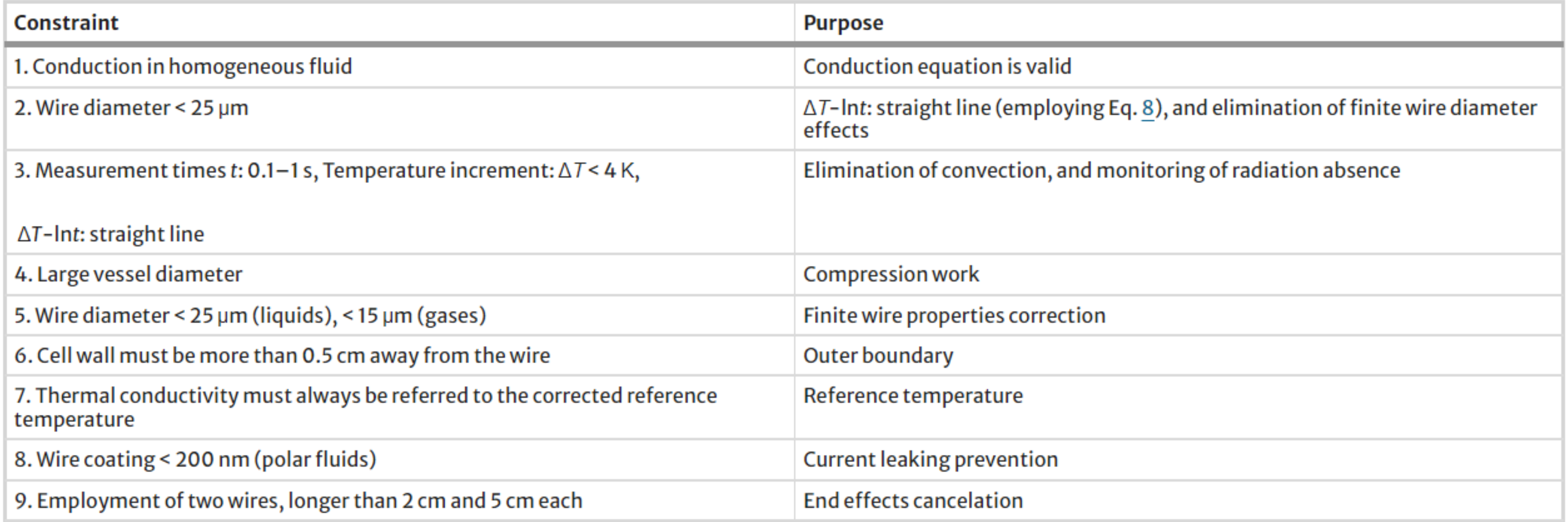




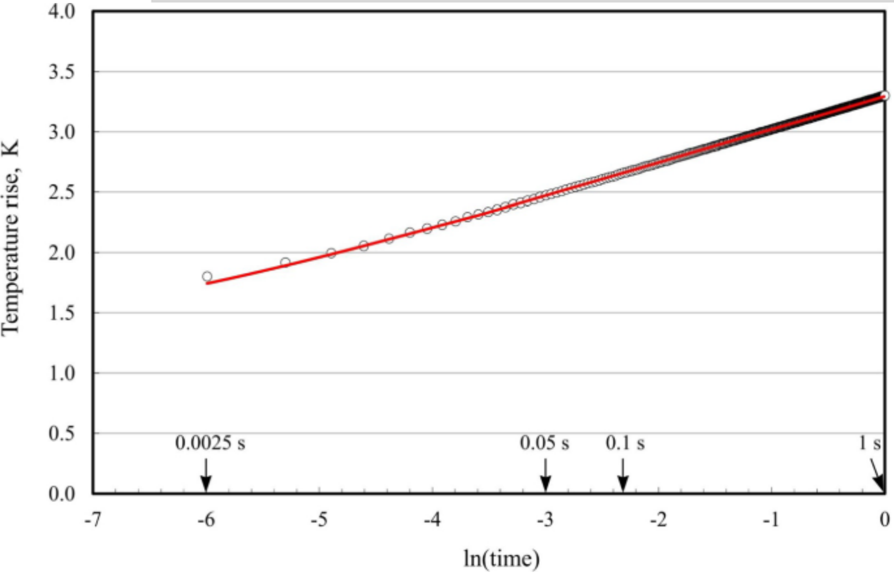
Thanks and apologies to Toni

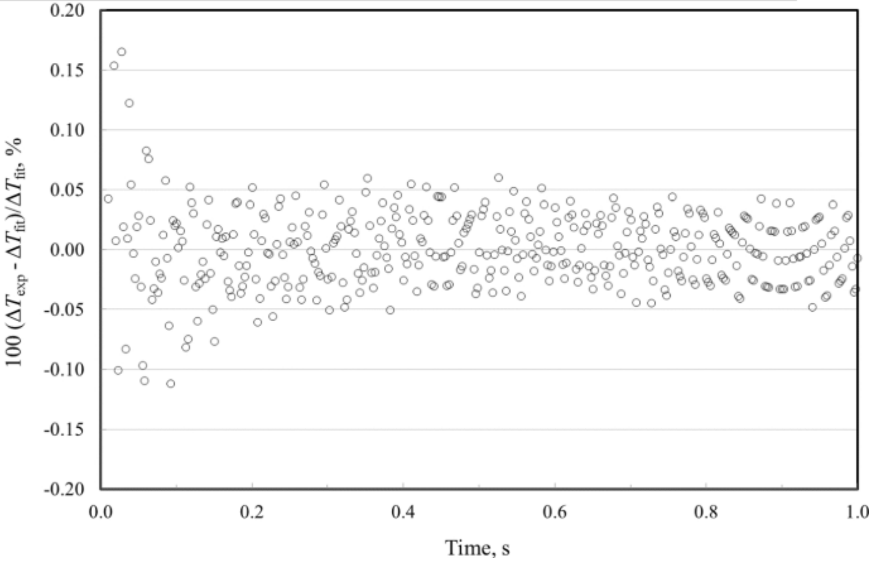
What makes it high fidelity

Assael, Marc J., et al. *International Journal of Thermophysics* 44.6 (2023): 85.



Constraint	Purpose
1. Conduction in homogeneous fluid	Conduction equation is valid
2. Wire diameter < 25 μm	ΔT–ln$t$: straight line (employing Eq. 8), and elimination of finite wire diameter effects
3. Measurement times t: 0.1–1 s, Temperature increment: ΔT < 4 K, ΔT–ln$t$: straight line	Elimination of convection, and monitoring of radiation absence
4. Large vessel diameter	Compression work
5. Wire diameter < 25 μm (liquids), < 15 μm (gases)	Finite wire properties correction
6. Cell wall must be more than 0.5 cm away from the wire	Outer boundary
7. Thermal conductivity must always be referred to the corrected reference temperature	Reference temperature
8. Wire coating < 200 nm (polar fluids)	Current leaking prevention
9. Employment of two wires, longer than 2 cm and 5 cm each	End effects cancelation

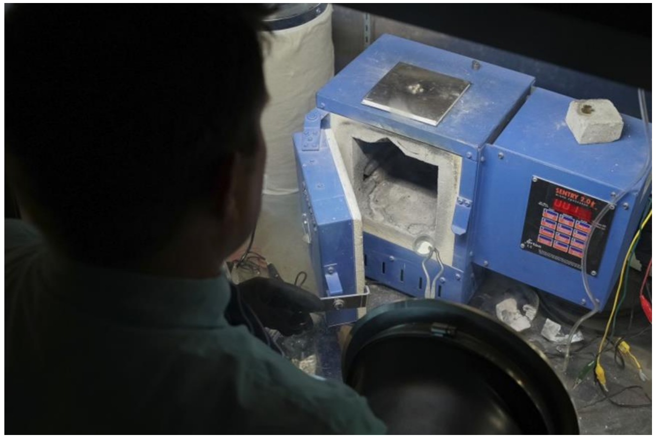




Summary

Summary

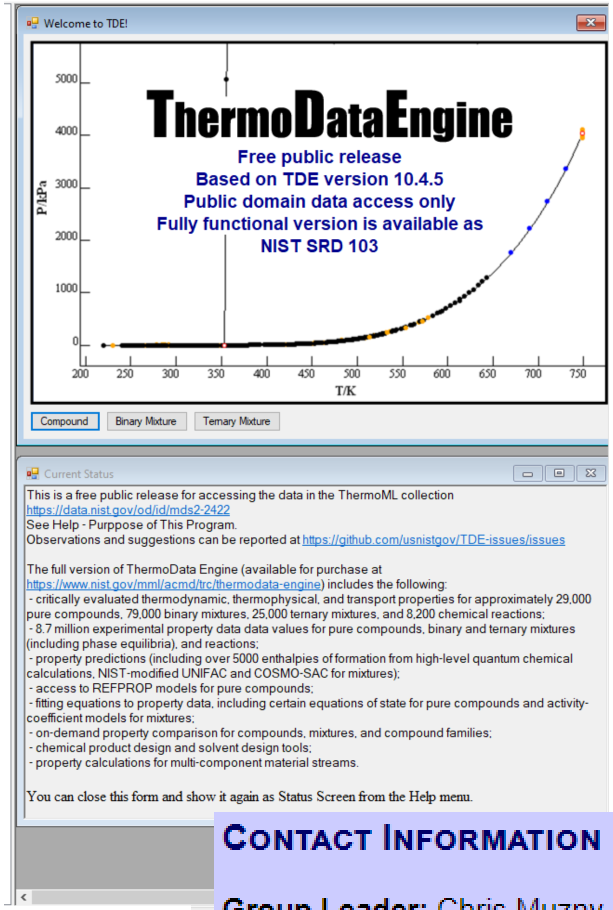
- Thermal conductivity and thermal diffusivity are difficult to measure
  - No standard measurement methods or reference liquids
  - Data scatter is too much to decisively decide the dk/dT relationship
- Using a complement of techniques can begin to bound uncertainties and overcome challenges when no standards exist
  - Experiments must match high-fidelity models to capture all heat transfer physics
- As a community, we're starting to fill the gaps with some binary and ternary mixtures
  - Unary salt properties are still needed as well as many other studies



NOTE: NIST Thermodynamic Research Center (TRC)

- From NIST “the best service we could offer is collaboration with motivated authors **<u>to prepare machine-readable data publications</u>**, exposing them in the public domain, and gradual improvement of the infrastructure and procedures.”
- MSTDB-TP is great, but it contains correlation instead of raw data
- This NIST database can be really complementary helpful because it presents the raw data

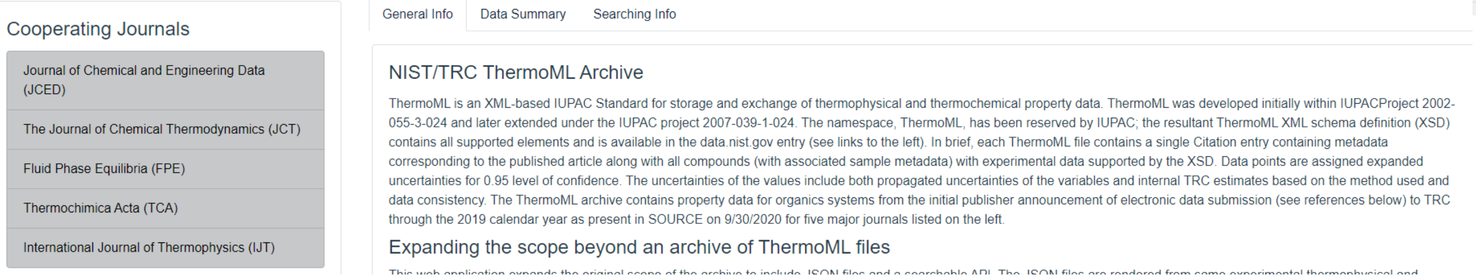
https://trc.nist.gov/



This is a free public release for accessing the data in the ThermoML collection
https://data.nist.gov/od/id/mds2-2422
See Help - Purppose of This Program.
Observations and suggestions can be reported at https://github.com/usnistgov/TDE-issues/issues

The full version of ThermoData Engine (available for purchase at https://www.nist.gov/mml/acmd/trc/thermodata-engine) includes the following:
- critically evaluated thermodynamic, thermophysical, and transport properties for approximately 29,000 pure compounds, 79,000 binary mixtures, 25,000 ternary mixtures, and 8,200 chemical reactions;
- 8.7 million experimental property data data values for pure compounds, binary and ternary mixtures (including phase equilibria), and reactions;
- property predictions (including over 5000 enthalpies of formation from high-level quantum chemical calculations, NIST-modified UNIFAC and COSMO-SAC for mixtures);
- access to REFPROP models for pure compounds;
- fitting equations to property data, including certain equations of state for pure compounds and activity-coefficient models for mixtures;
- on-demand property comparison for compounds, mixtures, and compound families;
- chemical product design and solvent design tools;
- property calculations for multi-component material streams.

You can close this form and show it again as Status Screen from the Help menu.



NIST/TRC ThermoML Archive

ThermoML is an XML-based IUPAC Standard for storage and exchange of thermophysical and thermochemical property data. ThermoML was developed initially within IUPACProject 2002-055-3-024 and later extended under the IUPAC project 2007-039-1-024. The namespace, ThermoML, has been reserved by IUPAC; the resultant ThermoML XML schema definition (XSD) contains all supported elements and is available in the data.nist.gov entry (see links to the left). In brief, each ThermoML file contains a single Citation entry containing metadata corresponding to the published article along with all compounds (with associated sample metadata) with experimental data supported by the XSD. Data points are assigned expanded uncertainties for 0.95 level of confidence. The uncertainties of the values include both propagated uncertainties of the variables and internal TRC estimates based on the method used and data consistency. The ThermoML archive contains property data for organics systems from the initial publisher announcement of electronic data submission (see references below) to TRC through the 2019 calendar year as present in SOURCE on 9/30/2020 for five major journals listed on the left.

Expanding the scope beyond an archive of ThermoML files

This web application expands the original scope of the archive to include JSON files and a searchable API. The JSON files are rendered from some experimental thermophysical and

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Thank You

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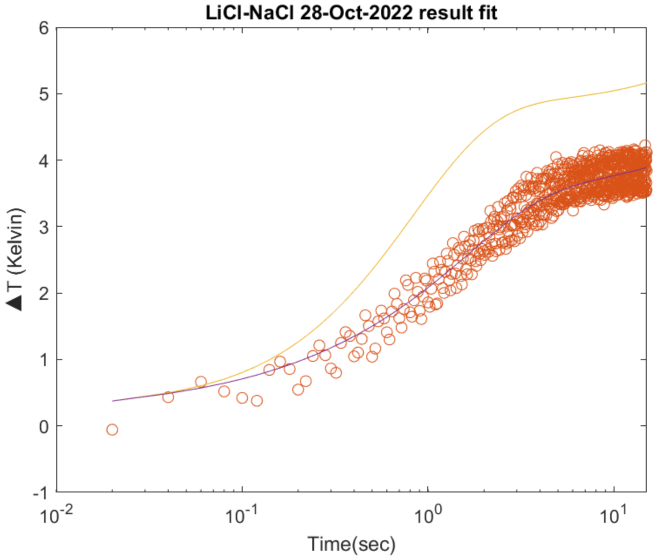
Specific sources of uncertainty

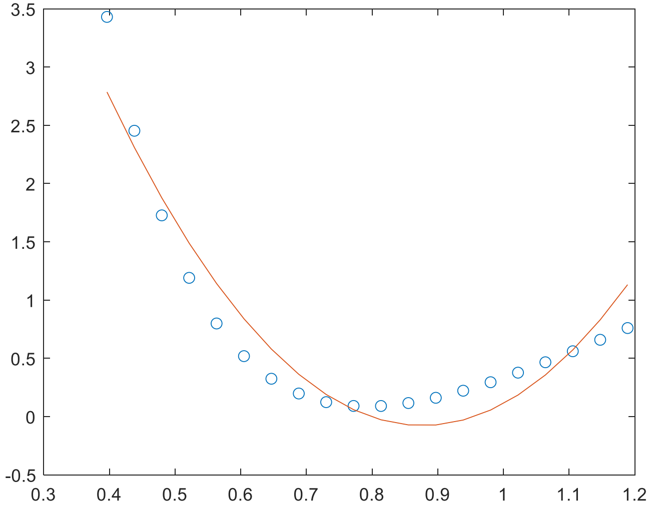
Our current uncertainty quantification involves 4 main sources of error:

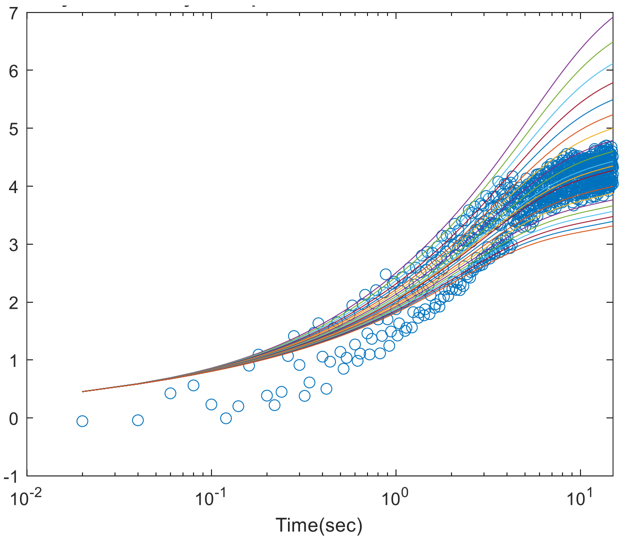
1) Goodness of fit error of the model to experimental data and other system biases.
2) Corrections based on measurements compared to standard reference materials (i.e. water) and FEM.
3) Propagation of the uncertainty from every parameter in the analysis model.
4) Variance in measurements.

Curve Fitting

- Thermal conductivity and diffusivity values are varied and a non-linear least squares fit is used
- Evaluate χ^2 error



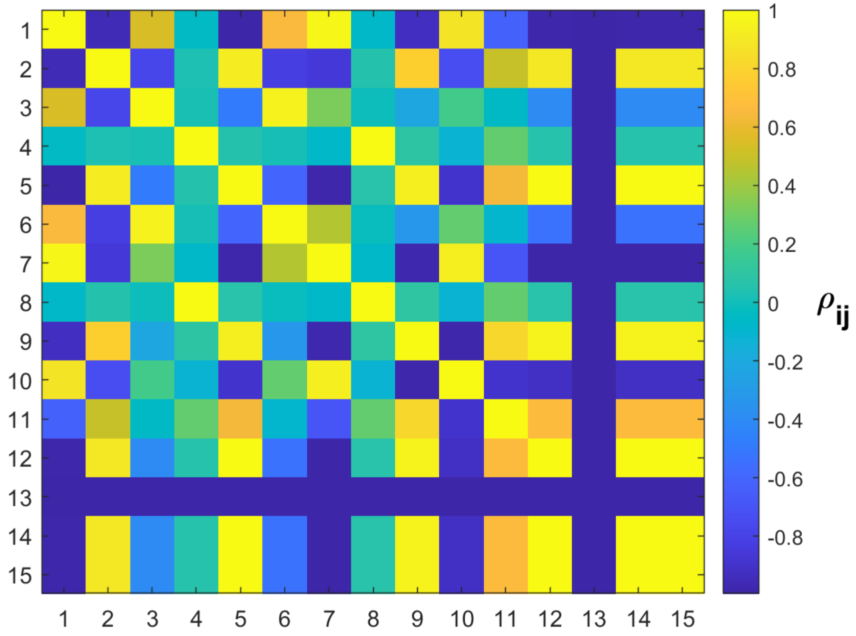




Correlated Parameters

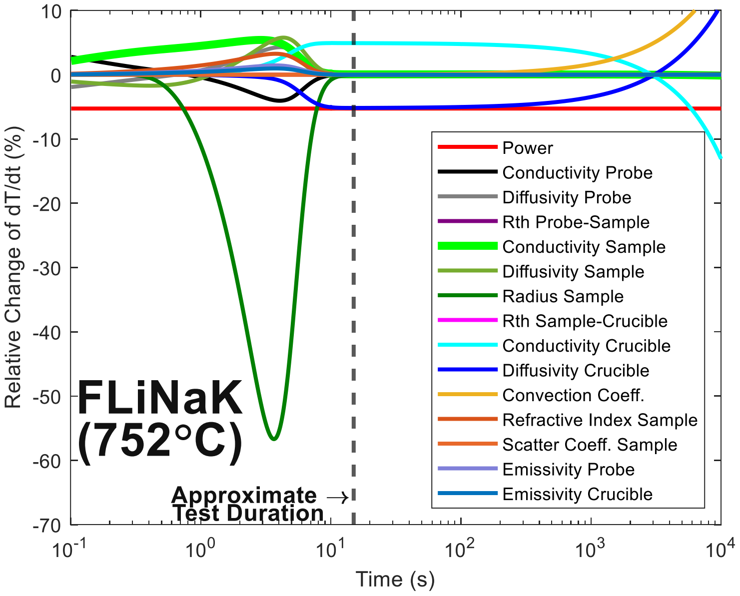
Use Pearson coefficients to determine which model parameters are directly correlated

$$\rho_{ij} = \frac{\int_0^t [\frac{df(t)}{dp_i} \cdot \frac{df(t)}{dp_j}]\, dt}{[(\int_0^t (\frac{df(t)}{dp_i})^2\, dt) \cdot (\int_0^t (\frac{df(t)}{dp_j})^2\, dt)]^{1/}}$$

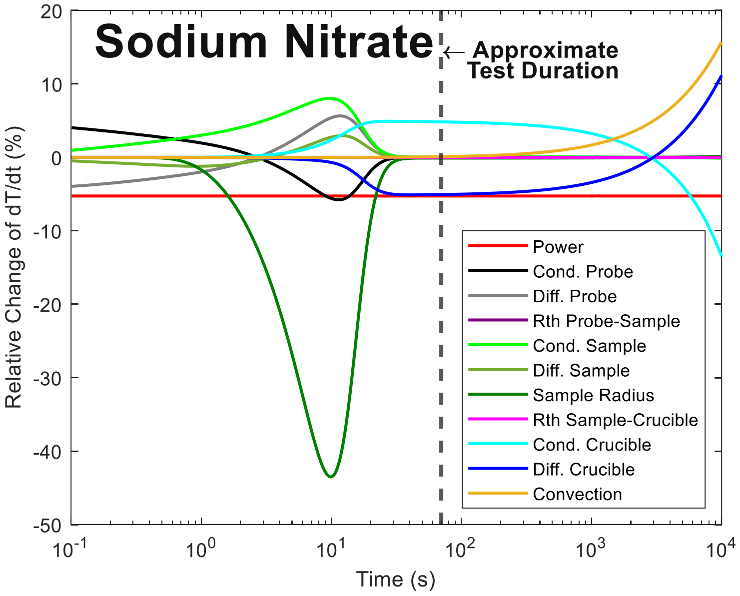


1) ϕ_0, 2) k_{probe}, 3) α_{probe}, 4) R_{c1-2}, 5) k_{sample}, 6) α_{sample}, 7) r_{sample}, 8) R_{c2-3}, 9) $k_{crucible}$, 10) $\alpha_{crucible}$, 11) h, 12) n, 13) ξ, 14) ϵ_{probe}, 15) $\epsilon_{crucible}$.

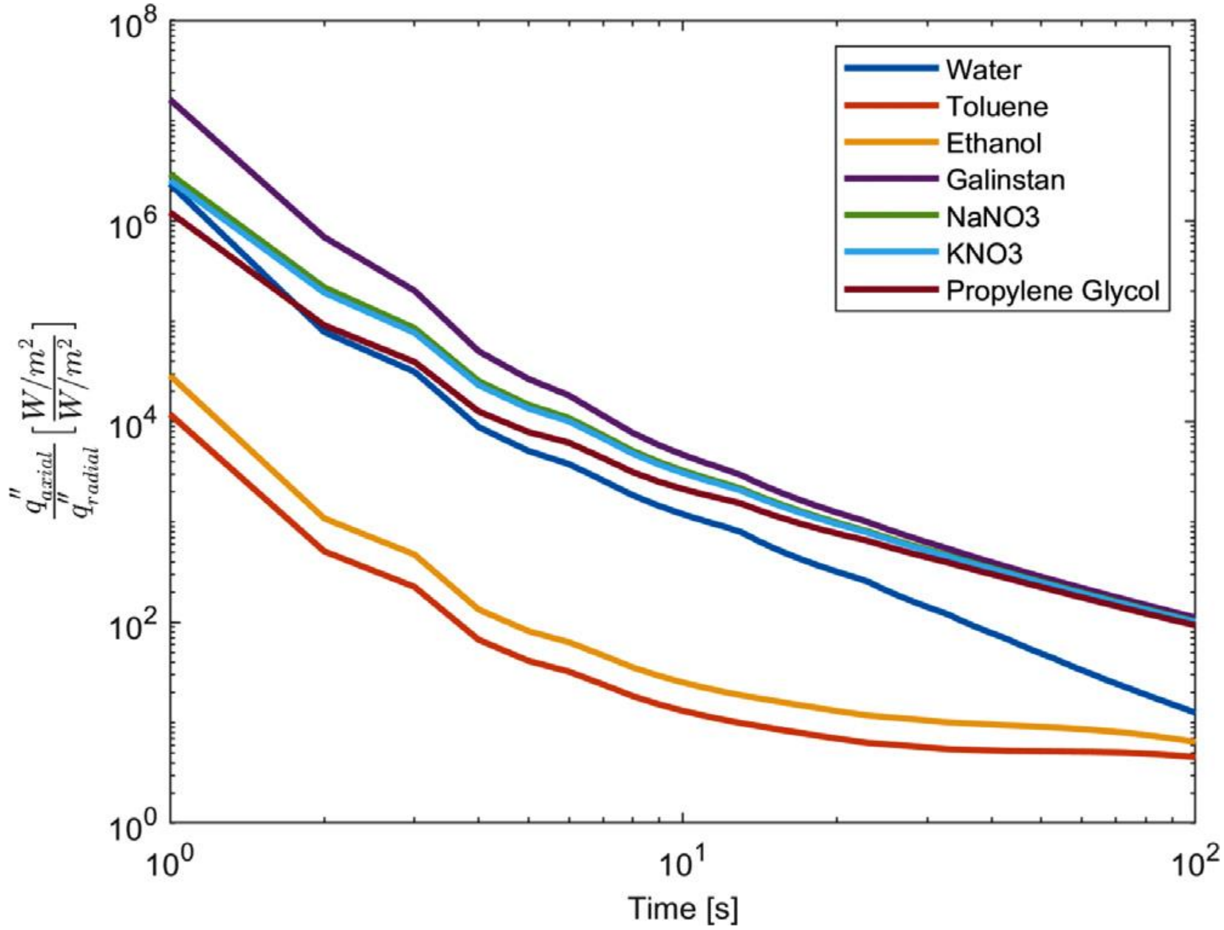
Sensitivity Analysis



Merritt [3]



Radial compared to axial heat transfer



Propagation of uncertaion

ANALYTICAL MODEL REFINEMENT

$$q_r = \frac{[T(0) - T(e)]4n^2\overline{\sigma}T_0^3}{(\varepsilon_0^{-1} + \varepsilon_e^{-1} - 1 + \xi e)}$$

$$\theta^* = T^* - T_0^* = \frac{T - T_0}{Q\rho^{-1}c^{-1}e^{-1}}$$

$$q_r^* = \frac{\theta(0) - \theta(e)}{T_0^*(\varepsilon_0^{-1} + \varepsilon_e^{-1} - 1 + \xi e)}$$

$$N_{Pl} = \frac{\lambda \beta_e}{4n^2\overline{\sigma}T_0^3}$$

$$q_r^* = \frac{q_r}{4n^2\overline{\sigma}T_0^4}$$

$$q_r = \frac{[T(0) - T(e)]4n^2\overline{\sigma}T_0^3}{(\varepsilon_0^{-1} + \varepsilon_e^{-1} - 1 + \xi e)}$$

$$q_r = \frac{\Delta T}{R_r}$$

$$R_r^* = T_0^*(\varepsilon_0^{-1} + \varepsilon_e^{-1} - 1 + \xi e)$$

$$R_r = \frac{\varepsilon_0^{-1} + (\varepsilon_e^{-1} - 1) + \xi e}{4n^2\overline{\sigma}T_0^3}$$

RADIATION TERM

$$R_r = \frac{\varepsilon_{probe}^{-1} + [(\varepsilon_{crucible}^{-1} - 1) + \xi(r_{sample} - r_{probe})](\frac{r_{probe}}{r_{sample}})}{4n^2\overline{\sigma}T_0^3\Gamma_{probe}}$$

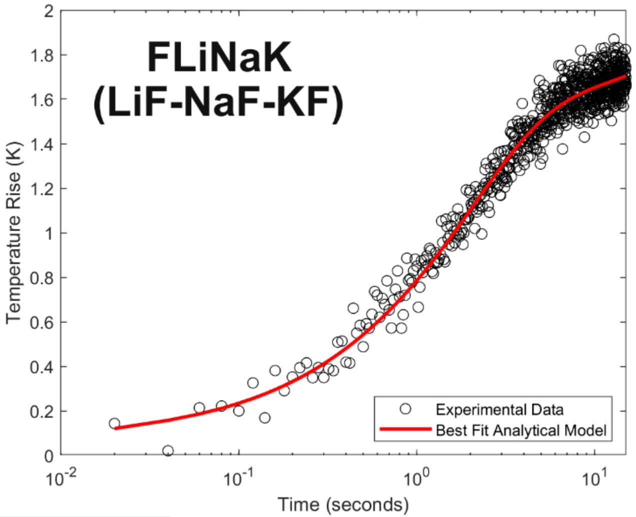
$$\begin{bmatrix} \theta_{inner} \\ \phi_{inner} \end{bmatrix} = \begin{bmatrix} A_{cr} & B_{cr} \\ C_{cr} & D_{cr} \end{bmatrix} \begin{bmatrix} \theta_{outer} \\ \phi_{outer} \end{bmatrix}$$

$$A_{cr} = \frac{B_c + A_c R_r}{B_c + R_r}$$

$$B_{cr} = \frac{B_c R_r}{B_c + R_r}$$

$$C_{cr} = \frac{A_c + D_c + C_c R_r - 2}{B_c + R_r}$$

$$D_{cr} = \frac{B_c + D_c R_r}{B_c + R_r}$$



NEW GOVERNING EQUATION

$$\begin{bmatrix} \theta_0 \\ \phi_0 \end{bmatrix} = \begin{bmatrix} A_{c,1} & B_{c,1} \\ C_{c,1} & D_{c,1} \end{bmatrix} \begin{bmatrix} 1 & R_{c1-2} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} A_{cr,2} & B_{cr,2} \\ C_{cr,2} & D_{cr,2} \end{bmatrix} \begin{bmatrix} 1 & R_{c2-3} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} A_{c,3} & B_{c,3} \\ C_{c,3} & D_{c,3} \end{bmatrix} \begin{bmatrix} 1 & 0 \\ h\Gamma_{crucible} & 1 \end{bmatrix} \begin{bmatrix} \theta_4 \\ \phi_4 \end{bmatrix}$$