Berkeley Nuclear Engineering
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Round Robin 1.0 for Molten Salt Chemical and Thermal Properties Characterization

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Lecco, YMSR conference

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NEUP Nuclear Energy University Program
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Round Robin| Organization

Organized by:

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UC Berkeley graduate student: Christian Sclafani
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U.of S.Carolina, Ted Bessman

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Alessio Thorpe (El Toro High School, Lake Forest, CA)
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The SALT Group | Organizers

SALT.nuc.berkeley.edu

Elemental analysis & spectroscopy

Graphite. Tritium. Tribology.

Electrochemistry Fluoroacidity

Corrosion

Rheology. Elemental analysis.

Mechanical design.

PH.D. STUDENTS

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Salt loops. Corrosion in salt loops.

Lorenzo Vergari

Electrochemical sensors.

Haley Williams

Salt speciation. Optical basicity, rheology.

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Data science.

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Contact angle.

UNDERGRADUATE RESEARCHERS

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User interface for sensors.

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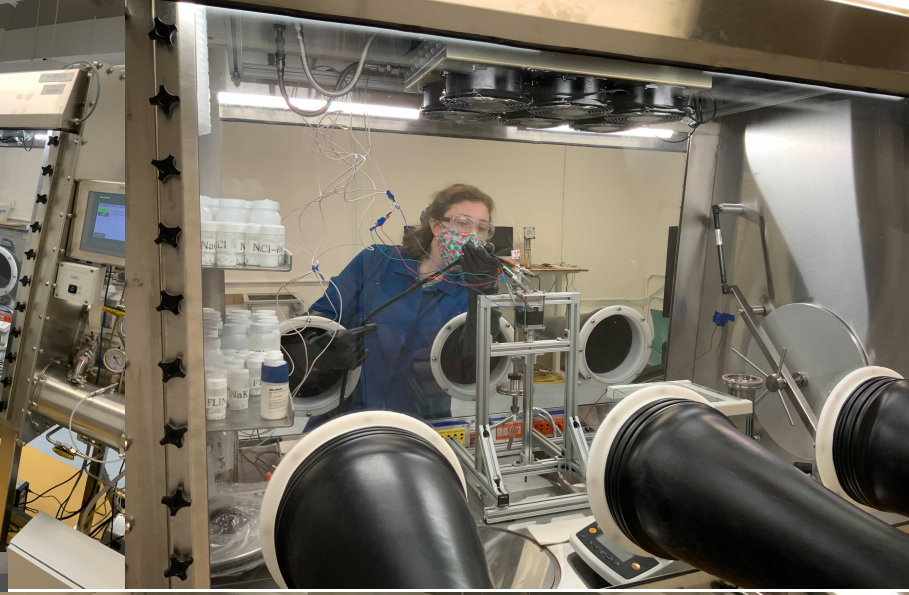
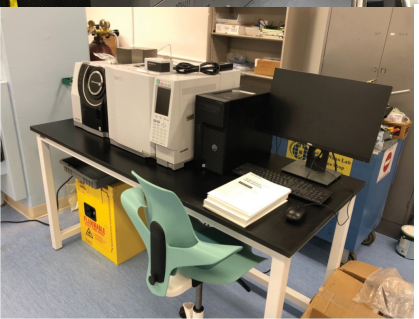


Landfill

Monte Carlo
MONACO



Round Robin

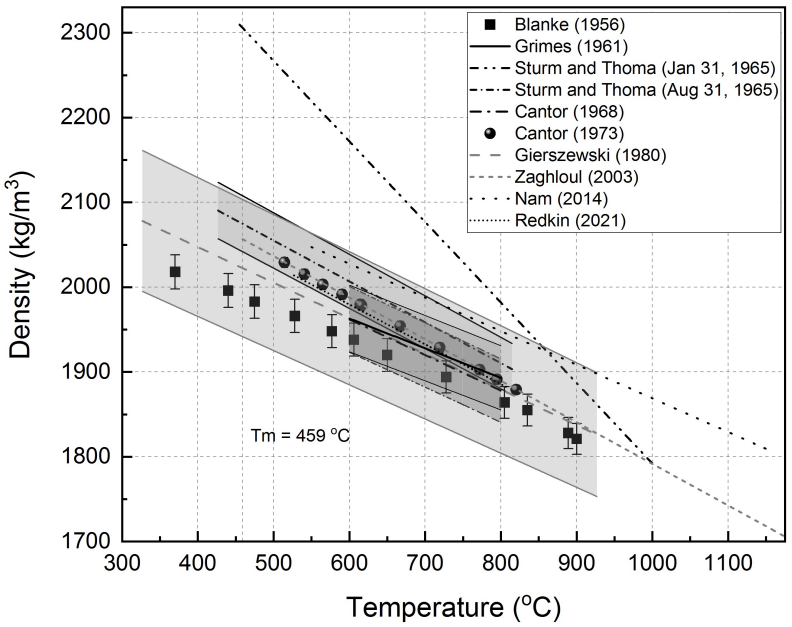
"In experimental methodology, a round robin test is an interlaboratory test performed independently several times. This can involve multiple independent scientists performing the test with the use of the same method in different equipment, or a variety of methods and equipment."

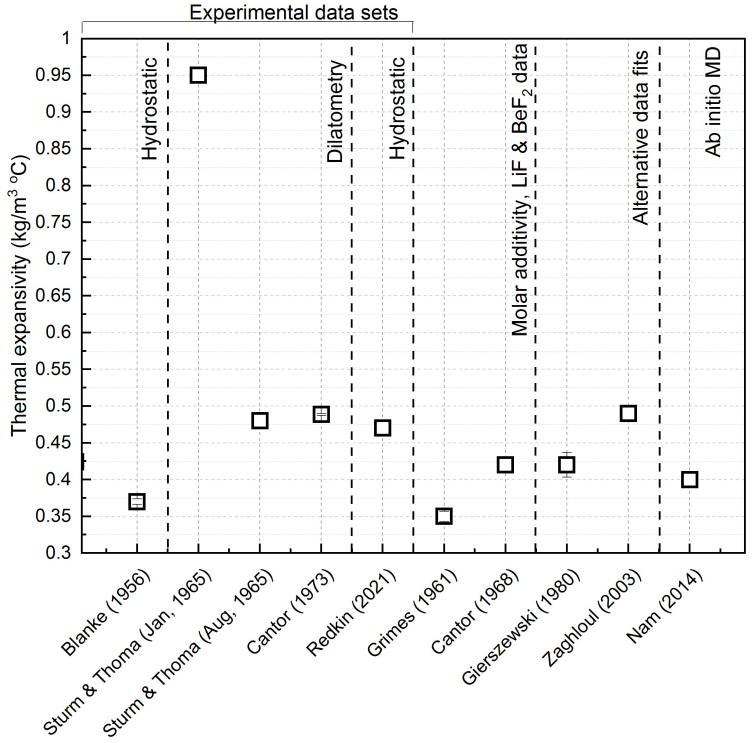
Pierson R. H., Fay E. A. (December 1959). "Guidelines for Interlaboratory Testing Programs". *Analytical Chemistry*. **31** (12): 25A–49A

Motivation for the Round Robin | FLiBe density variability

The variability among the prior data for the liquid density of FLiBe is 11% and for the thermal expansivity of FLiBe it is 61%.

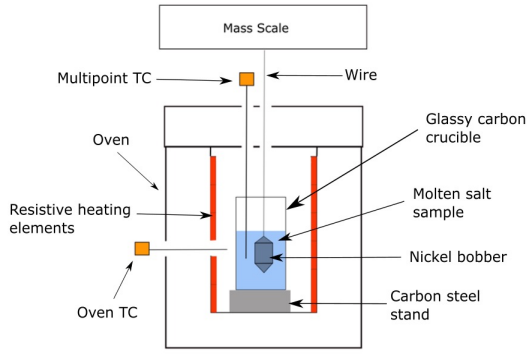
- It is not possible to assess if this variability is within the measurement error of the studies since the uncertainty in prior density data is not always reported
- no studies report the measurement uncertainty on the thermal expansivity

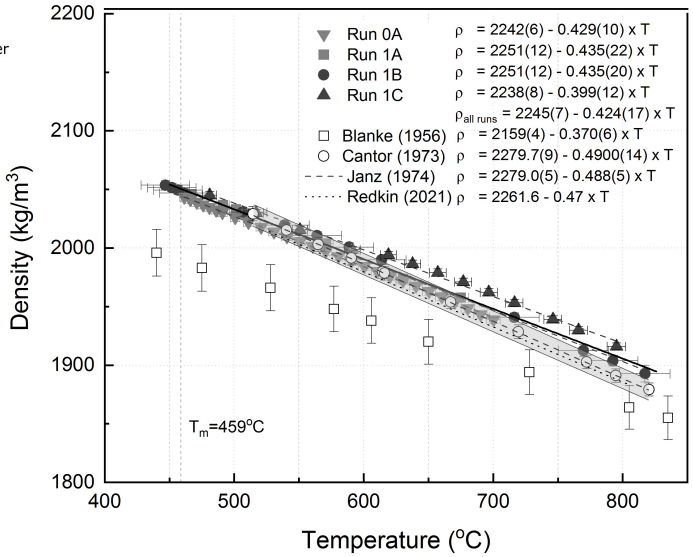


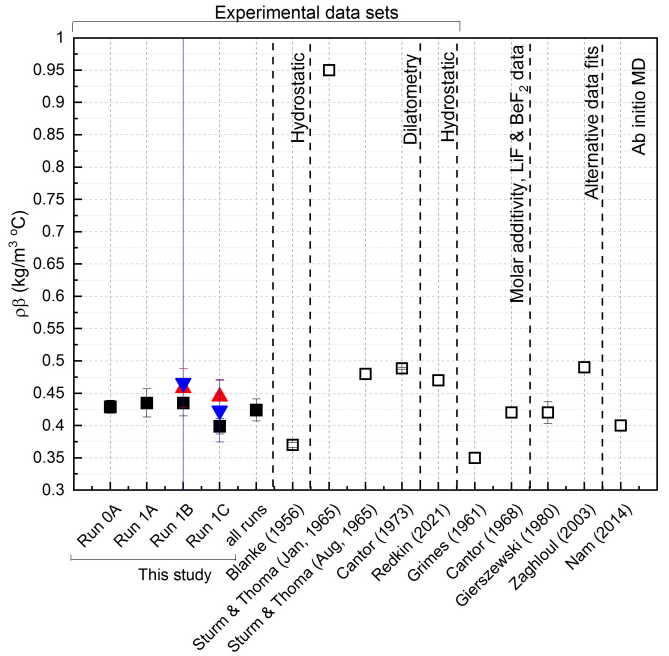


Sara Mastromarino*, Ricardo Vidrio*, Evan Still, Louis Chapdelaine, Raluca O. Scarlat
Measurements and Uncertainty Quantification for the Density and Coefficient of Thermal Expansion of Molten 2LiF-BeF2 (FLiBe). (Journal of Engineering Data, 2022)

Motivation for the Round Robin | FLiBe density measurement







The liquid density of FLiBe is measured to be:

ρ_{FLiBe} =2245(7) – 0.424(17) T

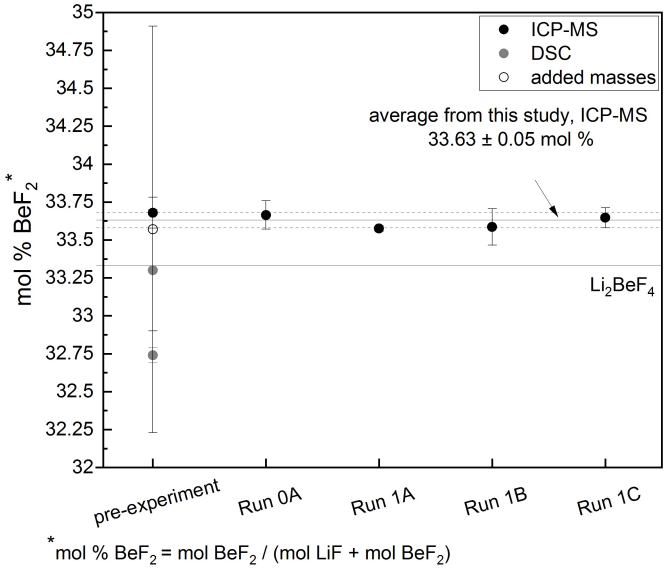
over the range of 447 °C to 820 °C,

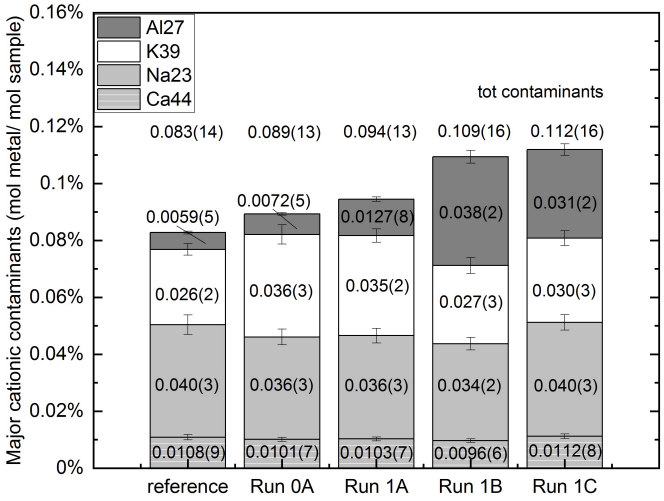
at 33.63(5) mol% BeF_2

- measurement accuracy: 0.3% for density, 4% for thermal expansivity
- **uncertainty** in thermal expansion of the bobber and volume of the bobber, **uncertainty** in surface tension on the wire and measurement **uncertainty** for temperature and mass

Motivation for the Round Robin | Elemental analysis

FLiBe sampled before density measurements (reference) and after each run





sources of variability :

salt composition (0.1%), salt contaminants (2%), Li isotopic composition (2%), sample isothermal conditions (0.2%), dissolved gases (<0.3%), and evolution of bubbles with temperature transients (depending on which cover gas 0.1 to 0.6% for dilatometry, and 1 to 5% for hydrostatic measurements).

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Overview of Molten Salt Round Robin 1.0

Salts used: NaCl-KCl (50:50 mol %) and FLiNaK
Purified by: Oak Ridge National Laboratory
Shipped to: UC Berkeley (shipped in plastic vials sealed with parafilm, sealed inside of glass jars)
Distributed to participants: stored in Ar glove-box at UC Berkeley; shipped overnight to participants when they were ready receive them (packaged as above)

Fig. 1. Salt samples prepared by ORNL, stored in Argon glove box at UC Berkeley. Nov. 2020.

Timeline

Participant recruiting meeting: July 15th, 2020 (defining RR1 goals)
Purified salts received from ORNL: Nov. 2021
Meeting 1: Nov. 12th, 2020 (prior to method submission & sample distribution)
Meeting 2: Apr. 8th, 2021 (prior to method peer review submission & data submission)
Meeting 3: TBD – purpose: finalizing RR1 report

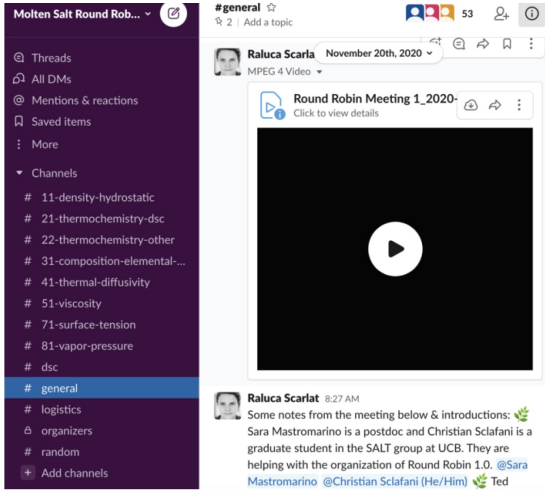


Fig. 2. Snapshot of communication platform for Molten Salt RR1

Overview of Molten Salt Round Robin 1.0

Objectives

1. Quantify **error:** identify sources of error, demonstrate reproducibility, identify limitations of measurement techniques
2. Share of best practices across the experimental groups, working towards **standard methodology**
3. Establish Establish **standard materials:** two well-characterized salt lots and can serve as reference material going forward.

Apart from the requirement of measuring the samples as received, no further restrictions or guidelines were given to the participants to avoid significant impact on the specific approaches of the participants. The performance of the measurements and analysis of the raw data, as well as data interpretation, were entirely at the responsibility of each single operator or operating team.

Participants to the Molten Salt Round Robin 1.0

Table 1. Planned contributions based on RR1 sign-up form. Feb. 2021.

Property Measurement	Measurement Method	Number of Participants
Density	Hydrostatic	7
	Displacement	1
	Pump Probe Spectroscopy	1
Elemental Composition/ Identification	ICP-MS/OES	5
	LECO	1
	LIBS	2
	Electrochemistry	2
Thermochemistry	Calorimetry	14
	Electrochemistry	2
	High Temp XRD	1
Thermal Conductivity	Laser Flash	3
	Pump Probe Spectroscopy	1
	Hot Wire	2
	Variable Gap	1
Viscosity	Falling Ball	2
	Rotational/ Torsional	4
	Pump Probe Spectroscopy	1
	Capillary Rise	1
Vapor Pressure	Knudsen Cell	1
	Pump Probe Spectroscopy	1
Surface Tension	Sessile Drop	2
	Maximum Bubble Pressure	1
	Pump Probe Spectroscopy	1
Others	Speed of Sound	1
	Electrical Conductivity	1

TOT Possible measurements: 59

Fig. 3. Registered participants based on RR1 sign-up form. Feb. 2021.
22 organizations
7 countries: USA (14 groups), Canada (3), Germany (1), Czech Republic (1), Netherlands (1), Denmark (1), Slovakia (1)

Table 2. Distributed salts as of June 2021.
22 organizations, 6 countries

Institute	Researchers	Salt Received
INL	Ruchi Gakhar, Michael Woods	50 g
UC Berkeley	Raluca Scarlat	100 g
LANL	Marisa Monreal	20g
Ontario Tech University	Markus Piro	5 g
University South Carolina, Chemistry	Hanno Zur Loye	15 g
North Carolina State University	Alex Bateller	100 g
Polytchnique de Montreal	Jean-Philippe Harvey	5 g
Washington State Univeristy	Xiaofeng Guo	50g
Wisconsin State Laboratory of Higiene	Sean Scott	5 g
Abilene Christian University	Kim Pamplin, Alli Mae Berry	105 g
UCSD	Jian Zeng	30 g
BYU	Troy Munro	100 g
Canadian Nuclear Laboratories	Mouna Saoudi	10 g
ANL	Melissa Rose	200 g
ORNL	Ryan Gallagher, Abbie McAllister, Jake McMurray	215 g
Penn State	Nathan Smith	210 g
BYU	Matt. Memmott, Kent Detrick	525 g
ONRL	Abbey McAlister	3g
ITU, Karlsruhe	Ondej Benes	25g
Rez Institure, Czech Republic	Martin Straka	240 g
Copenhagen Atomics	Thomas Steenberg	20 g
University South Carolina	Ted Bessman	20 g
TU Delft	Anna Smith	10g

Table 3. Method procedures and data sets received. 70% of participants agreed to participate in blind-blind peer review of methods. Data submitted by Aug. 15th, 2021.

Property or Method	Methods Received (as of April 6th)	Data Sets Received (as of Aug 15th, 2021)
Density	7	4
Thermochemistry	15	7
Composition	5	4
Thermal Conductivity	6	1
Viscosity	3	0
Others (surf. Tension)	4	1

Example Procedure Template

SALT PROPERTY MEASUREMENT METHOD

For instructions, see also MS Round Robin Form 2: https://forms.gle/C1ddLiQ733xyshNE6

Purpose of this document:
(1) To identify your salt-sample needs.
(2) To collect methodology details so that appropriate data submission protocols are generated for each sub-group.
(3) Optional: to provide the opportunity for blind-blind reciprocal peer review of experimental methodologies prior to data collection.

Logistics:
a) Please enter your participant ID above. Do not enter any other identifying information.
b) Please fill in each box below and delete the example blue text.
c) Please fill in ***a separate document for each property*** being measured.
d) Please submit this document via From 2: https://forms.gle/C1ddLiQ733xyshNE6

1 PROPERTY BEING MEASURED

liquid density (ρ)

2 SALT SAMPLE

2.1 How is the sample prepared for loading into the measurement instrument?

The as-shipped jar is brought into an inert glove-box.

The salt is removed from its two containers (glass jars and plastic vial), and ground for homogenization in an agate mortar and pestle.

~40 g of salt powder is loaded in a crucible used for liquid density measurements.

2.2 How much salt is needed per sample? How many samples will be analyzed?

One analysis requires 40 g of salt. We will analyze a duplicate of samples.
We need a total of 50 g of salt. (to allow for some salt lost)

3 EXPERIMENTAL METHOD: A BRIEF DESCRIPTION

The hydrostatic method is used. A nickel plummet of known weight and volume is immersed in the molten salt. Its immersed weight is measured by an analytical balance. The salt crucible is kept in an oven, and temperature is varied upwards and downwards. Measurements are taken when they system has reached thermal equilibrium. The plummet is cleaned in before measurement of a new, to avoid salt contamination. A new crucible is used in each new kind of salt to avoid salt contamination.

Table 1. Relevant experimental parameters

Parameter	Values covered
Temperature	from melting point (or lowest achievable temperature in supercooled state) to 1000°C (instrument limit), in increments of 50°C. Measurements should be taken in random order (i.e. 450°C, 800°C, 650°C)
Temperature transient	Both heating and cooling transients will be observed and measured.

Table 2. Data recorded during an experimental run

Recorded data & file format	Notes, and calibration (when applicable)
weight of sample set-up before and after experiments	Salt + bobber + crucible + wire (to check for weight losses or gains during experimentation)
diameter of wire	Measured by micrometers and recorded
CSV file with weight vs. temperature	Scale calibration using accredited metrology laboratory. Temperature calibration performed using a dry block calibrator.
Weight of bobber	Scale calibration by accredited metrology.
Volume of bobber	Room-temperature bobber volume calibration with fluids of NIST-traceable density.
Photos of frozen salt sample at the conclusion of the experiments	Dimensional and color scale card included in the photo.
Gas composition in the glove-box during measurements	Which gas (Ar, N2 etc), and H2O and O2 levels. Sensors were calibrated by the glove-box vendor.
Material certification reports	Verify material purity/composition
Weight of the wire	

4 SAMPLE STORAGE

Table 3. Samples Generated and Fate of Samples

Type of sample	Fate/Notes
Part of the as-received unground salt left in the shipping container.	Stored in the glove-box until conclusion of Round Robin 1.0. Then kept in the group for future unrelated experiments, or discarded.
Left over ground salt.	Available for other MS Round Robin measurements. Stored in a sealed container in an inert glove-box.
Post-measurement salt samples, removed from their crucible as solid chunks.	Available for other MS Round Robin measurements. Stored in a sealed container in an inert glove-box.
Wire used for hanging bobber	Discarded
Salt crucibles and bobbers	Washed and re-used

5 DATA REDUCTION & ERROR ANALYSIS

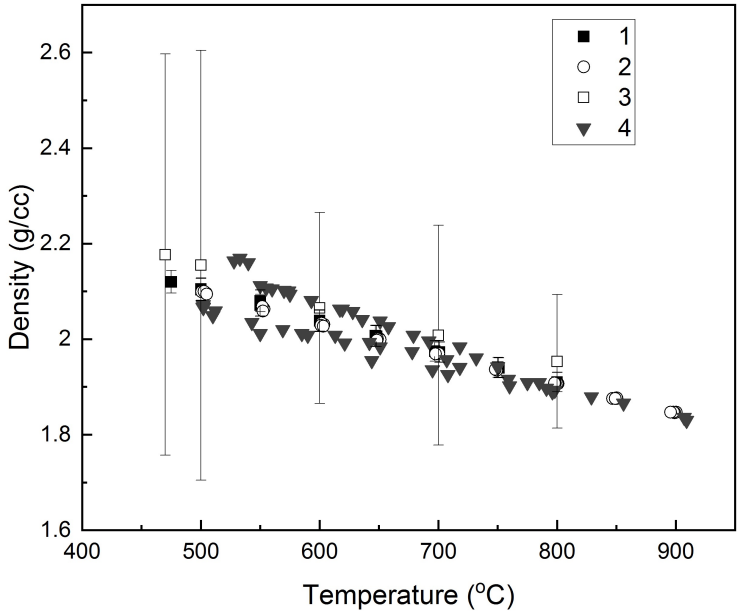
Table 4. Inputs into data reduction and uncertainty quantification

Input	Error analysis notes
Weight vs. temperature	Repeatability is considered: several heat and cool cycled on the same sample. Reproducibility is considered: sample duplicates are prepared.
Surface tension of salt, wire diameter	Measured force corrected for surface tension on wire.
Bobber weight	Measurement uncertainty determined by the balance used.
Bobber volume	Determined using calibration fluids. Error on calibration fluid density is propagated to bobber volume error.
Salt wetting up wire	The wire will be visually inspected for residue of wetting up the wire

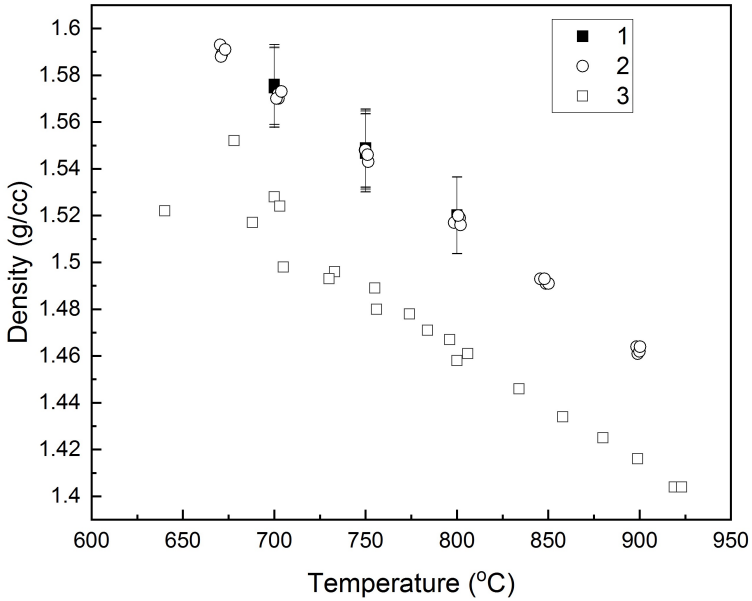
Molten Salt Round Robin 1.0 | https://salt.nuc.berkeley.edu/round-robin/
UC Berkeley | Oak Ridge National Laboratory | University of South Carolina | Molten Salt Thermal Properties Working Group (MSTPWG)

Round Robin | Density measurement: 4 submissions

FLiNaK



NaCl-KCl



Participant ID	Technique	Calibration Method	What was reported?	What was not Reported?	Notes:
122RR1	Hydrostatic	Archimedian bobber volume calibration method, balanced checked against another balance (calibrated using calibration weights)	Temperature, bobber Volume @25C, bobber volume at Temperature, bobber volume calibration log, wire diameter, Photos of crucibles and bobber.	Uncertainty	
132RR1	Hydrostatic	Archimedian bobber calibration using calibration fluids, NIST weights used for scale calibration, fluke thermocouple calibration	Temperature, Density, Uncertainty		
169RR1	Hydrostatic	Archimedian bobber volume calibration, scale calibration using NIST weights, thermocouple calibration done by 3 independent temperature measurements	Crucible volume, bobber material, bobber weight, salt weight, temperature range, density	Uncertainty	
179RR1	Hydrostatic	Archimedian bobber volume calibration method using NIST calibration fluids, balance calibrated using accredited metrology laboratory, temperature calibration performed using dry block calibrator.	Temperature, Density, Uncertainty		Salt type not specified. Only one data set resulted. Error quantification method not specified.

Notes/lessons learned:

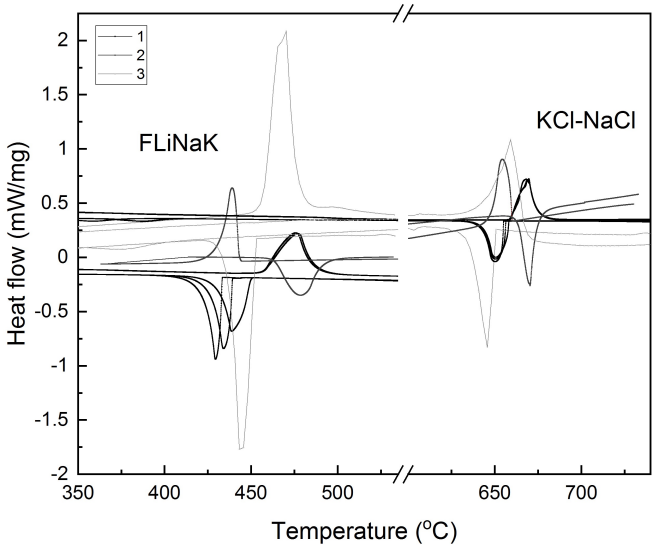
1. Calibration is important
2. error quantification

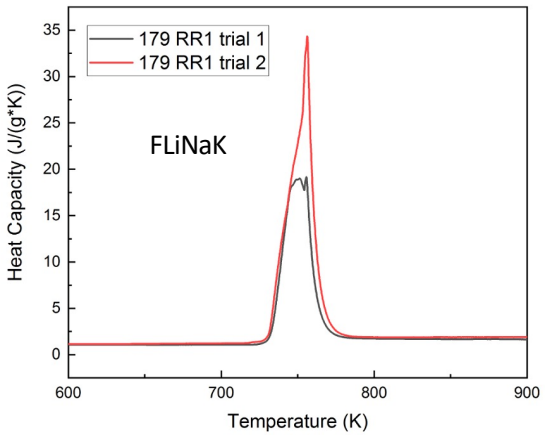
Round Robin| Melting point measurement: 7 submissions

#	Melting point	
	Temperature (ºC)	
	FLiNaK	NaCl-KCl
1	459.9	657.7
2	457(3)	659(3)
3	457.92	658.1
4	456.75	657
5	464.6(4)	660.6(1)
6	452.45	652

Notes/lessons learned:

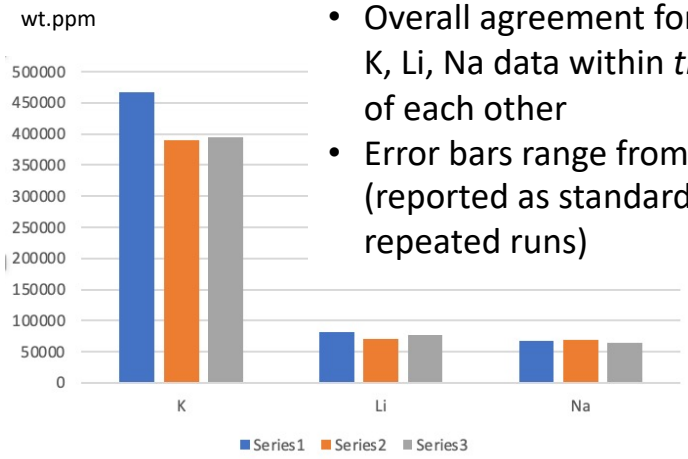
1. Place for raw data submission
2. Place for fully reduced data submission.
3. Place to list what is included in the error quantification.
4. Place to upload raw data for calibration runs





Round Robin| Elemental analysis ICP-OES/MS

Isotope analyzed	172 RR1 ICP-OES		147RR1 ICP-MS		137 RR1-ICP OES/MS	
	Conc	st. dev.	Conc	st. dev.	Conc	st. dev.
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
K	467572	1225	390453	31185	395000	20000
Li	80897	45	71257	4320	77500	4000
Na	67378	36	68849	4961	64500	3000
Ni	4359	21	10.7	1.3		
Si	4205	311				
Mo	575	3	0.1	0.02		
Cr	454	2	4.1	0.4		
Zr	289.1	0.7	466	27		
Fe	285	3	3	0.2		
Cu	178.2	0.5				
P	175.7	0.2				
Ba	146.0	0.9	169	9		
Cs	135.2	0.8	0.02	0.002		
Ca	82	10	64	5		
Al	120	26	15	2	6.5	0.8
Y	98.2	0.4			<0.08	
Mg	45	4			21	1
Er	41.3	0.4	21	5		
Ce	35.2	0.2				
Ti	32.58	0.14				
Bi	28	3				
Sn	19.7	0.3				
Co	13.95	0.11				
Mn	4.97	0.02				
Gd	3.8	0.3				
Ag	2.788	0.012				
Ga	2.2	0.3				
W	1.90	0.15				
Au	68	2				
B					< 2	
Be	4.625	0.008				
Cd	94	13				
Dy						
Ge						
Hf						
La					<0.2	
Lu						
Nb						
Nd						
Os						
Pd						
Ru	71	3				
Se	128	6				
Sm						
Sr						
Te						
Tm	138	2				
V	35	5				
Zn						
Sc					<0.3	



- Overall agreement for major constituents: K, Li, Na data within *three standard deviations* of each other
- Error bars range from 0.1% to 8% uncertainty (reported as standard deviation among repeated runs)

Little agreement for minor constituents. e.g.:
4359(21) vs. 10.7(1.3) ppm for Ni
120(26) vs. 15(2) vs. 6.5(8) ppm for Al
289.1(0.7) vs. 466(27) ppm for Zr
454(2) vs. 4.1(0.4) ppm for Cr

Participant ID	Technique	Calibration Method	What was reported?	What was not Reported?
137RR1	ICP-MS	N/a	Chemical Composition, Elemental Impurities, Uncertainty	Calibration Technique
147RR1	ICP-MS	Solution calibration curve dilution, scale calibrated using weights, analytical balance accurate to 0.001	Chemical Composition, Uncertainty	N/a
172RR1	ICP-OES	Solution calibration curve dilution, scale calibrated using weights, analytical balance accurate to 0.001	Chemical Composition, Uncertainty	N/a

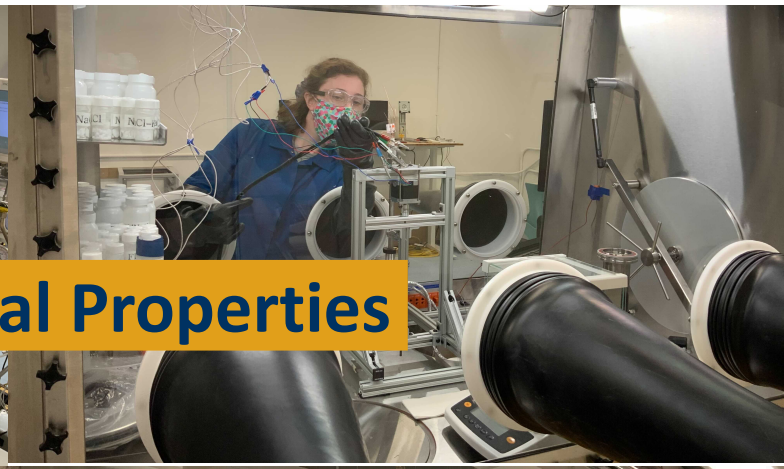
Round Robin | Summary - Observations

1. Overall: high interest from the community in participating. Time-consuming measurements.
2. Time-consuming coordination across many different types of measurements.
3. Overall: high variability in magnitude of error bars.
4. Elemental analysis: high-variability for minor constituents analysis.
5. Viscosity: 8 registered, no data submitted for RR1. Allow for more time?
6. Challenging to achieve full transparency of experimental and analysis method.

Round Robin | What was learned?

1. Large opportunity for growing the participant pool.
2. Participant poll indicated large interest & capability from participants to also perform measurement on Be-containing and U/Th-containing salts.
3. Generally: interest in participating in blind-blind method peer review.
4. Need to upload calibrations and standard materials used for calibrations.
5. Need to list what is included in the error quantification.
6. Need to standardize data submission format and data validation upon submission
7. Need to submit fully reduced data, along with raw data





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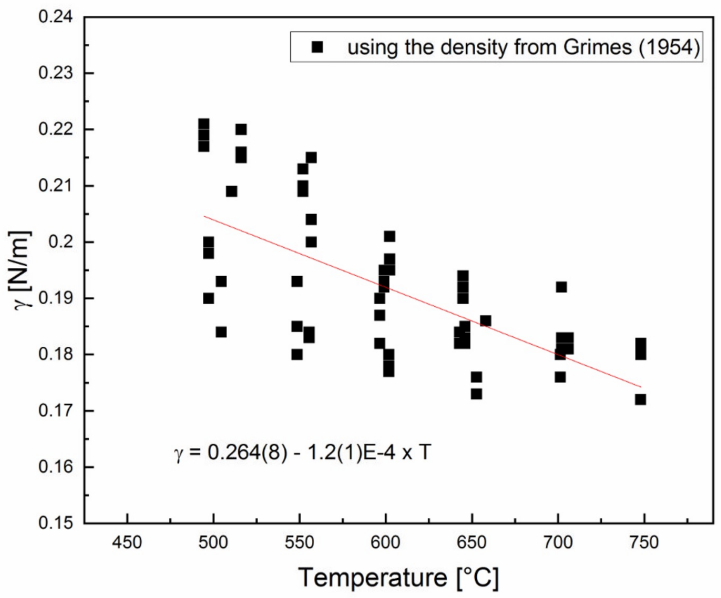
Department of Nuclear Engineering, University of California Berkeley

June 6th, 2022
Lecco, YMSR conference

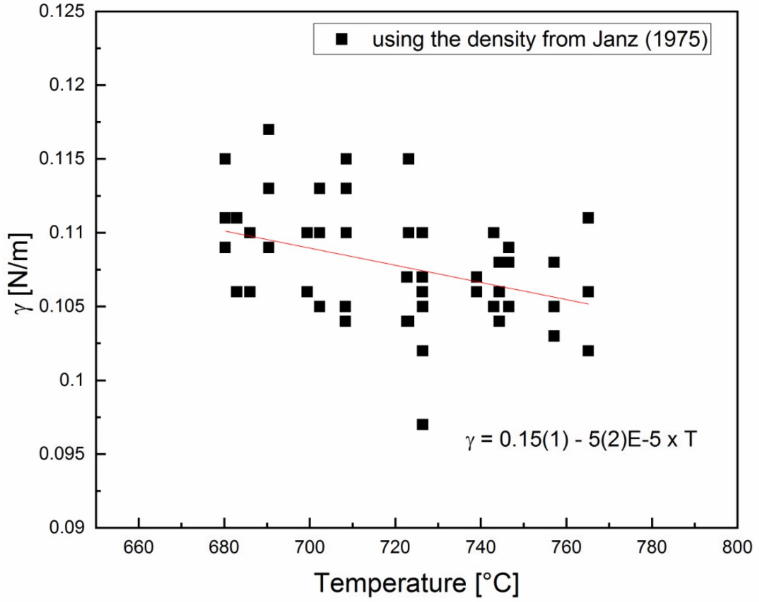


Round Robin | Surface tension Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA)

FLiNaK



NaCl-KCl



Participant ID	Technique	Calibration Method	What was reported?	What was not Reported?
122RR1	Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA)	N/a	Surface Tension, Contact Angle, and Densities were reported with uncertainties	Calibration method

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Round Robin | Thermal conductivity modulated photo-thermal radiometry (MPR)

NaCl-KCl

Temperature	Thermal conductivity	±
°C	W/m-K	W/m-K
690	0.45	0.054
690	0.45	0.051
690	0.49	0.057

Temperature	Thermal conductivity average[a]	±[b]
°C	W/m-K	W/m-K
690	0.46	0.057

[a]The average value is calculated based on the 3 individual measurements

[b]The uncertainty includes both systematic and random errors

FLiNaK

Temperature	Thermal conductivity	±
°C	W/m-K	W/m-K
500	0.65	0.066
550	0.69	0.072
600	0.66	0.067
500	0.63	0.064
550	0.65	0.068
600	0.67	0.069
500	0.65	0.084
550	0.64	0.065
600	0.65	0.067
650	0.65	0.067

Temperature	Thermal conductivity average[a]	±[b]
°C	W/m-K	W/m-K
500	0.64	0.083
550	0.66	0.071
600	0.66	0.069
650	0.65	0.067

[a]The average value is calculated based on the 3 individual measurements

[b]The uncertainty includes both systematic and random errors

Participant ID	Technique	Calibration Method	What was reported?	What was not reported?
166RR1	Modulated Photothermal Radiometry (MPR)	Pyrometer, vendor calibrated	Temperature, Average Thermal Conductivity k, Uncertainty	N/a