Gravimetric Water Vapor Permeability of Flat Materials and Finished Objects

Beyond Certification Under ISO 17025

L. Lundquist, C. Pelletier, Y. Wyser
Nestlé Research Center, Lausanne
Switzerland

Purpose

- Show dominant contributions to gravimetric WVTR uncertainty, depending on measurement procedure and measured barrier properties
- Limitations of the current method
- NOT discuss all contributions in detail

Outline

- WV-TR Method description
- Uncertainty: Causes & Relevant Effects
- Implications & Next steps

Samples

Vapor Barrier	Film	Rigid containers
HIGH	Metallized PET	Jar Co-E-P/EVOH/Co-E-P 
LOW	Pure PET	Beverage bottle PET/MXD-6/PET 

Method Flow Chart

Nestlé
Good Food, Good Life

Reference sealing

Only with small number of specimens

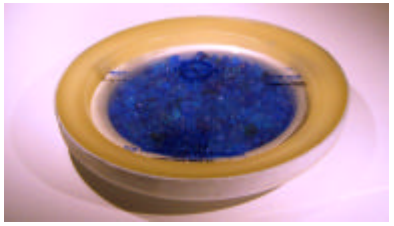
Volume measurement

Container sealing

Film dish sealing

Stabilisation climatic chamber

23°C
85% RH



Specimen

Blank Picture NA

Weighing, t_0

Weighing, t_{n-1}

48-96 hrs

Weighing, t_n

Blank

Specimen

1 month

The WVTR mathematical expression does not account for all sources of uncertainty

Nestlé
Good Food, Good Life

Method	Rigid container [mg/pack.day] Flexible film [g/m^2.day]
Blank (Films & Containers)	$WVTR = \frac{(m_n - m_{n-1}) - \{(m_n^b - m_{n-1}^b)\}}{A(t_n - t_{n-1})}$ Buoyancy Driving force Wall H_2O content
Reference vol. (Only Containers)	$WVTR = \frac{(m_n - m_{n-1}) - \{(m_n^r - m_{n-1}^r)(V_s/V_r)\}}{(t_n - t_{n-1})}$ Buoyancy

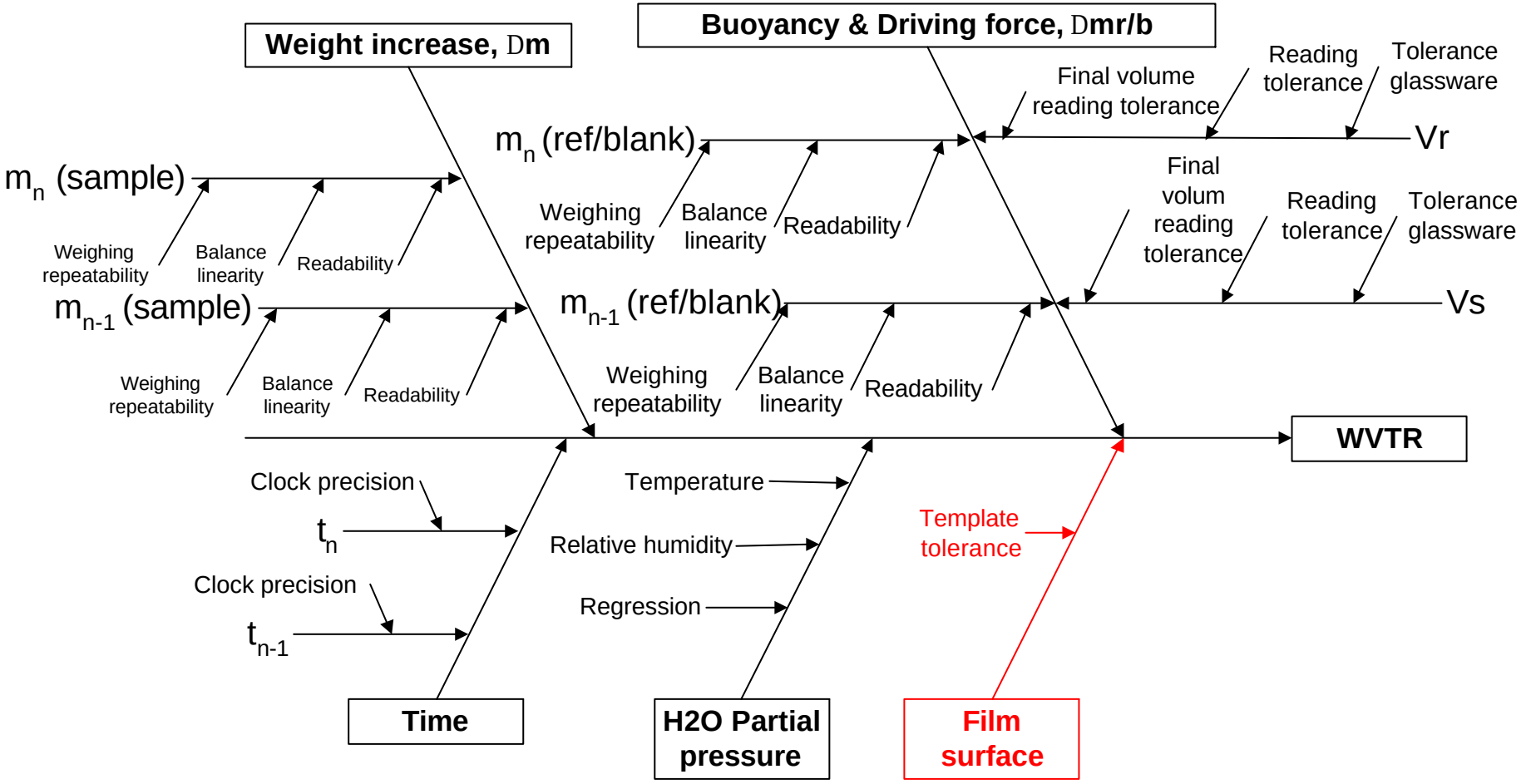
m = specimen mass [mg,g]
m^b = blank weight [mg,g]
m^r = reference weight [mg,g]

t = time [days]
V_s = sample volume [cm^3]
V_r = reference volume [cm^3]
A = film surface area [m^2]

Outline

- WV-TR Method description
- Uncertainty: Causes & Relevant effects
- Implications & Next steps

Cause & Effect Diagram



Weight change Dm/Dt, $Dm_{b,r}$/Dt

$$\frac{\Delta m}{\Delta t} = \frac{(m_n - m_{n-1})}{(t_n - t_{n-1})}$$

$u_{linearity}$ = 0.001g

$u_{readability}$ = 0.0002g

Sample (average of several specimens)

Repeatability Δm/Δt

$$u(\Delta m / \Delta t) = \frac{1}{\Delta t}\sqrt{SD_{rep}^{\,2} + 2*\left(\left(u_{linearity}\right)^2 + \left(u_{readability}\right)^2\right)}$$

Reference/blank (one specimen)

$$u(\Delta m_{r,b} / \Delta t) = \frac{1}{\Delta t}\sqrt{2*\left(\left(SD_{Balancerep}\right)^2 + \left(u_{linearity}\right)^2 + \left(u_{readability}\right)^2\right)}$$

Driving force is H_2O Partial pressure not RH

Good Food, Good Life

Climate

T= 23.4

u(T) = 0.3 °C

RH = 81.5

u(RH) = 0.8 %RH

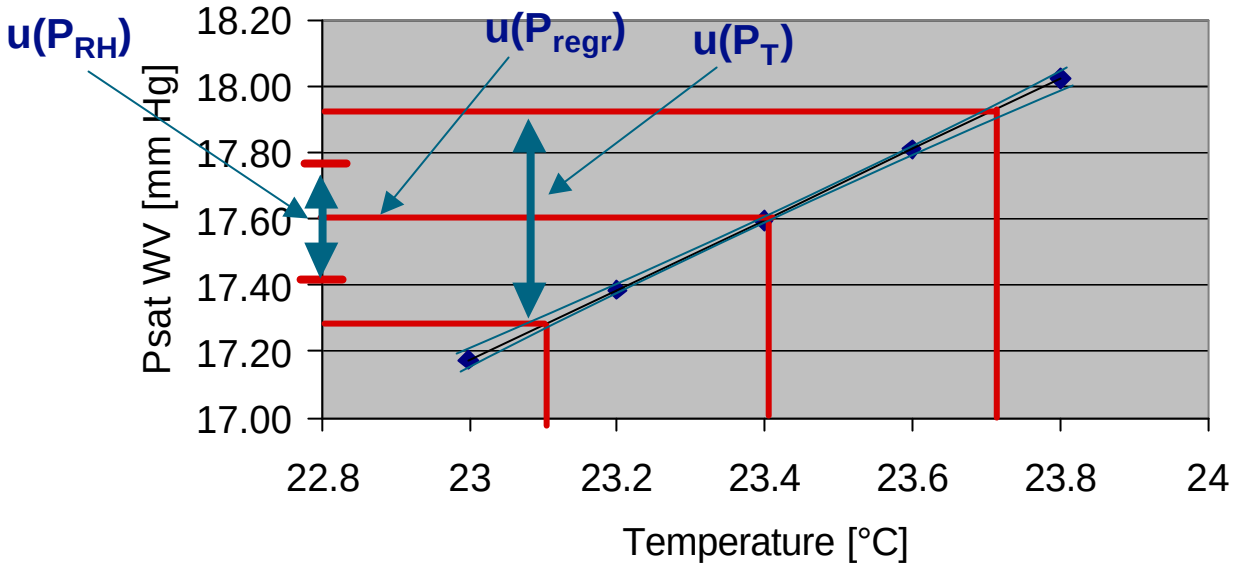
Driving force

$F \propto (P_{ext}-P_{int})$

$P_{int}= 0$

$P_{ext} = f(T,RH)$

$u(P_{RH}) = u(RH)*17.56$



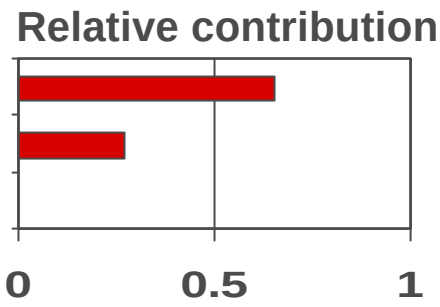
Source	uj	uj²	Rel contrib.
$u(P_{regr})$	0.0008	7.0E-07	5.5E-06
$u(P_T)$	0.31	0.095	0.75
$u(P_{RH})$	0.18	0.032	0.25
S (uj²)		**0.127**	
u_P	**17.56**	**0.36**	
Rel u_P	**1**	**0.02**	

Combined Uncertainty: Films

Nestlé
Good Food, Good Life

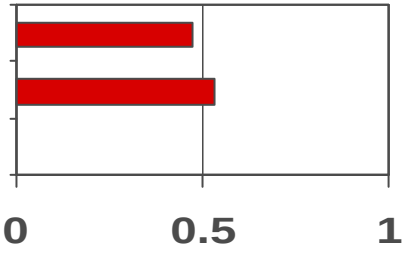
PET (low barrier)

Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	0.04	0.0022	199.9	0.2014	0.70
∆mb/dt	0.00	0.0015	-199.9	0.0851	0.30
A	0.005	0.00001	-1526.7	0.0005	0.00
Total (ciuj)^2				**0.287**	**1.00**
Total (ciuj) [g/m2.day]	**7.64**			**0.54**	
Relative (ciuj)				**0.07**	



Met-PET (high barrier)

Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	0.0017	0.0014	199.9	0.074	0.47
∆mb/dt	-0.0006	0.0015	-199.9	0.085	0.53
A	0.005	0.00001	-92.3	0.000	0.00
Total (ciuj)^2				**0.159**	**1.00**
Total (ciuj) [g/m2.day]	**0.46**			**0.40**	
Relative (ciuj)				**0.86**	

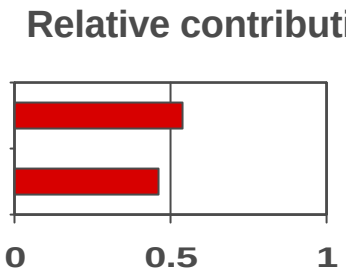


Combined Uncertainty: Rigid containers & Blank

Good Food, Good Life

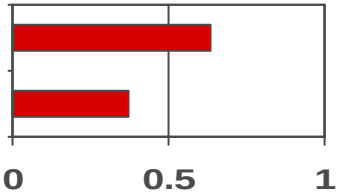
Bottle (low barrier)

Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	21.74	0.161	1	0.0258	0.54
∆mb/dt	0.29	0.147	-1	0.0217	0.46
Total (ciuj)^2				**0.047**	**1.00**
Total (ciuj) [mg/pack.day]	**21.45**			**0.22**	
Relative (ciuj)				**0.01**	



Jar (high barrier)

Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	1.21	0.190	1	0.0363	0.63
∆mb/dt	0.43	0.147	-1	0.0217	0.37
Total (ciuj)^2				**0.058**	**1.00**
Total (ciuj) [mg/pack.day]	**0.79**			**0.24**	
Relative (ciuj)				**0.31**	

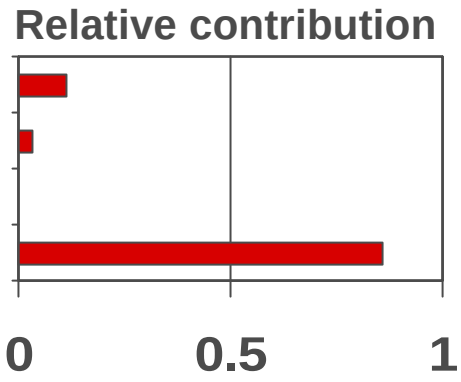


Combined Uncertainty: Rigid containers & Reference Volume

Good Food, Good Life

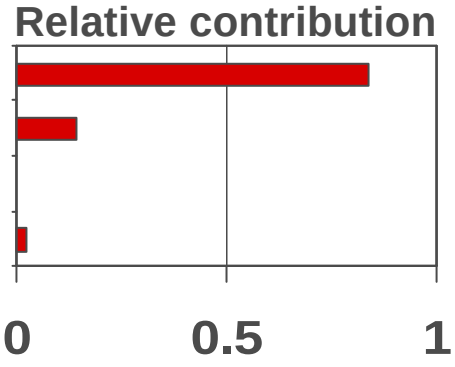
Bottle (low barrier)

Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	21.74	0.161	1	0.0258	0.11
∆mr/dt	-0.21	0.149	-0.53	0.0061	0.03
Vs/Vr	0.53	0.026	-0.21	0.0000	0.00
P H2O	1	0.02	21.85	0.1964	0.86
Total (ciuj)^2				**0.228**	**1.00**
Total (ciuj) [mg/pack.day]	**21.85**			**0.48**	
Relative (ciuj)				**0.02**	

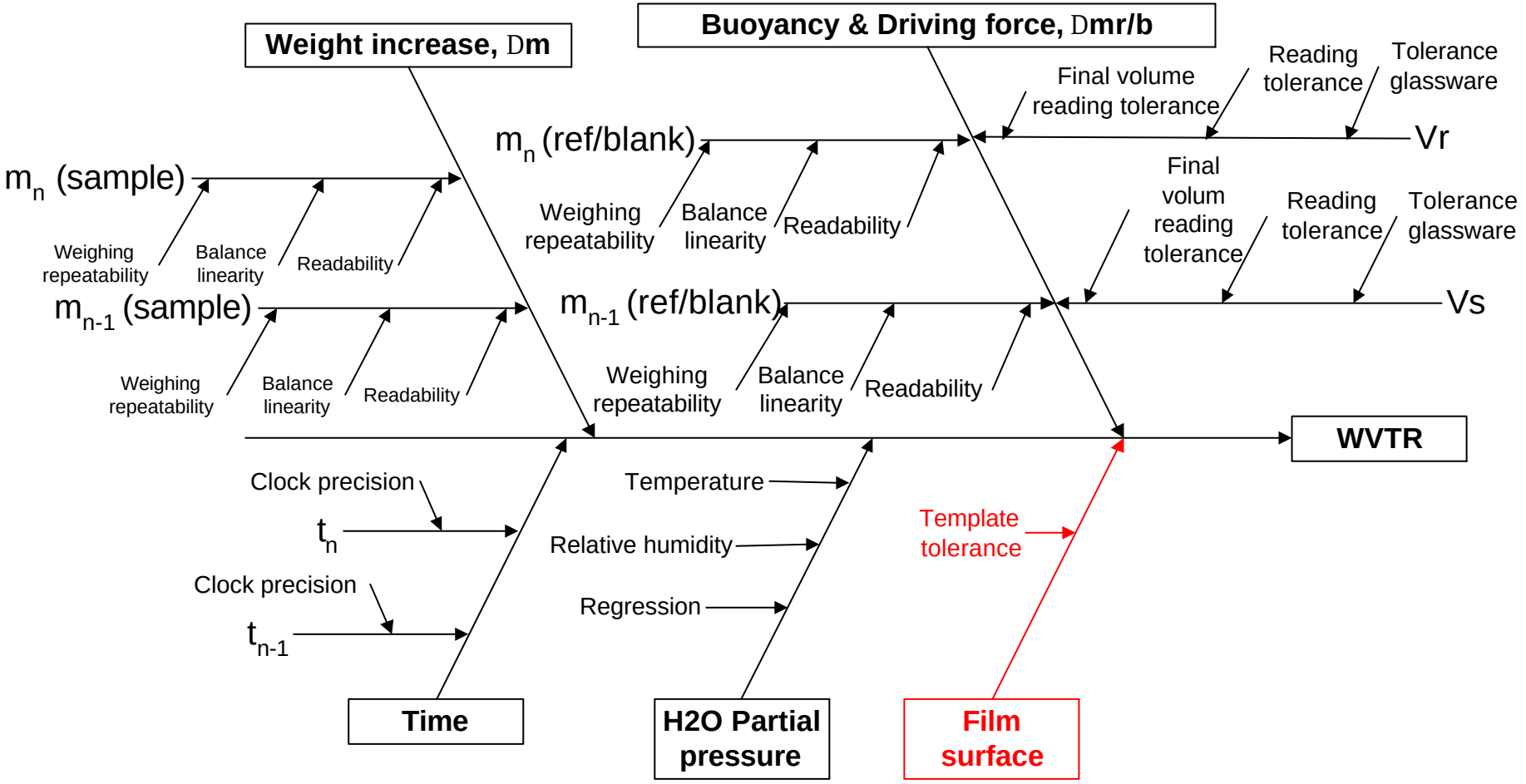


Jar (high barrier)

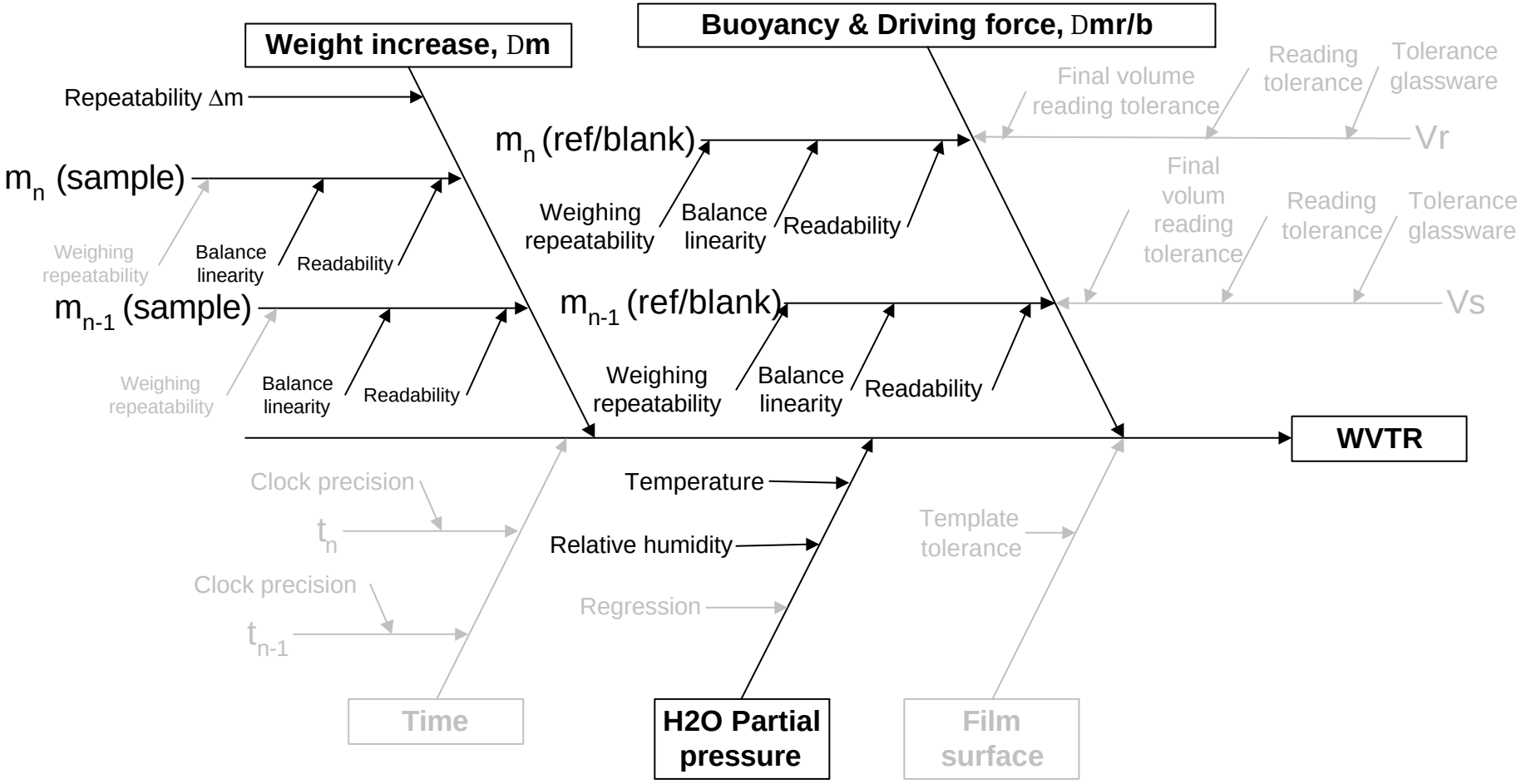
Source	Value	uj	ci	(ujci)^2	urel
∆m/∆t	1.21	0.190	1	0.0363	0.84
∆mr/dt	-0.21	0.149	-0.52	0.0060	0.14
Vs/Vr	0.520	0.026	-0.21	0.0000	0.00
P H2O	1	0.02	1.32	0.0007	0.02
Total (ciuj)^2				**0.043**	**1.00**
Total (ciuj) [mg/pack.day]	**1.32**			**0.21**	
Relative (ciuj)				**0.16**	



Cause & Effect Diagram



Refined Cause & Effect Diagram



Expanded Uncertainty Containers: Reference gives different result for low barriers

Nestlé
Good Food, Good Life

Barrier	Method	Value	Expanded uncertainty (k=2)	Comparison of means & variances 5% significance
LOW	Blank	21.45	0.98	NOT DIFFERENT
	Reference	21.85	0.96	
HIGH	Blank	0.79	0.48	DIFFERENT!
	Reference	1.32	0.42	

Outline

- WV-TR Method description
- Uncertainty: Causes & Relevant Effects
- Implications & Next steps

Implications & Next Steps

- Present method suited for low to medium barrier applications
  - MU for intermediate barriers
- Reference volume should be used with caution for medium to low barrier materials
- For reference volume method the climate control dominates uncertainty for low barriers, while remaining significant for high barriers
- Method improvement
  - Increase time-span between weighing not possible
  - Use balance with higher sensitivity
  - Linear regression over several measurements

Film surface area, A

D = 79.8 ± 0.2 mm

$$c_D = \frac{\partial}{\partial D}\left(\frac{p\,D^2}{4}\right) = \frac{p\,D}{2}$$

A [m2]	interval	distribution	uj	ci	ciuj
0.005	0.0002	rectangular	0.000115	0.12535	**1.45E-05**
				Urel	**0.003**

Sample volume/reference volume

Uncertainty of one volume measurement

Source	interval	distribution	uj	ci	ciuj	(ciuj)^2	urel
filling	20	rectangular	11.5	1	11.5	133	0.25
reading	20	rectangular	11.5	1	11.5	133	0.25
line marking	28	rectangular	16.2	1	16.2	261	0.49
Total (ciuj)^2						**528**	**1.00**
Total (ciuj)						**23.0**	

Expression

$$\frac{Vs}{Vr}$$

Sensitivity coefficients (ci) for combined uncertainty

$$\frac{\partial\left(\frac{Vs}{Vr}\right)}{\partial Vs} = \frac{1}{Vr} \qquad \frac{\partial\left(\frac{Vs}{Vr}\right)}{\partial Vr} = -\frac{Vs}{Vr^2}$$

Combined uncertainty beverage bottle, u(V)

Source	Value	uj	ci	(ujci)^2	urel
Vs	525	23.0	0.001	0.00053	0.78
Vr	1000	23.0	-0.000525	0.00015	0.22
Tot (ujci)^2				**0.001**	
Tot (ujci)	**0.525**			**0.026**	
Rel u(V)				**0.049**	