Uncertainty estimation of gravimetric water vapor permeability determination of flat materials and finished objects

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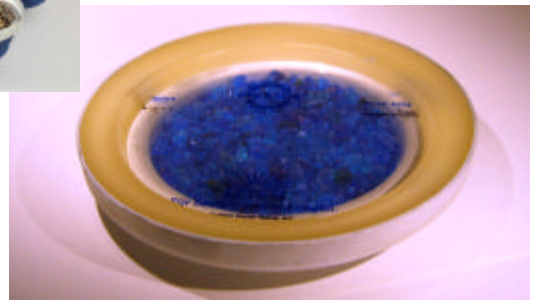
Why uncertainty?

- Accredited method with widespread use within Nestlé
- Enables comparisons between laboratories
- Enables comparisons with limits
- Knowledge about uncertainty permits appropriate material choice for packaging with respect to desired shelf life
- Highlights possibilities of method improvement

Samples

Vapor barrier	Film	Finished packs
HIGH	Metallized PET (Met-PET)	Jar Co-E-P/EVOH/Co-E-P 
LOW	Pure PET (PET)	Beverage bottle PET/MXD-6/PET 

Method Flow Chart



Container sealing → Volume measurement ← Reference sealing

↓

Film dish sealing → Stabilisation climatic chamber

23°C, 85% RH

↓

Weighing, t_0

↓

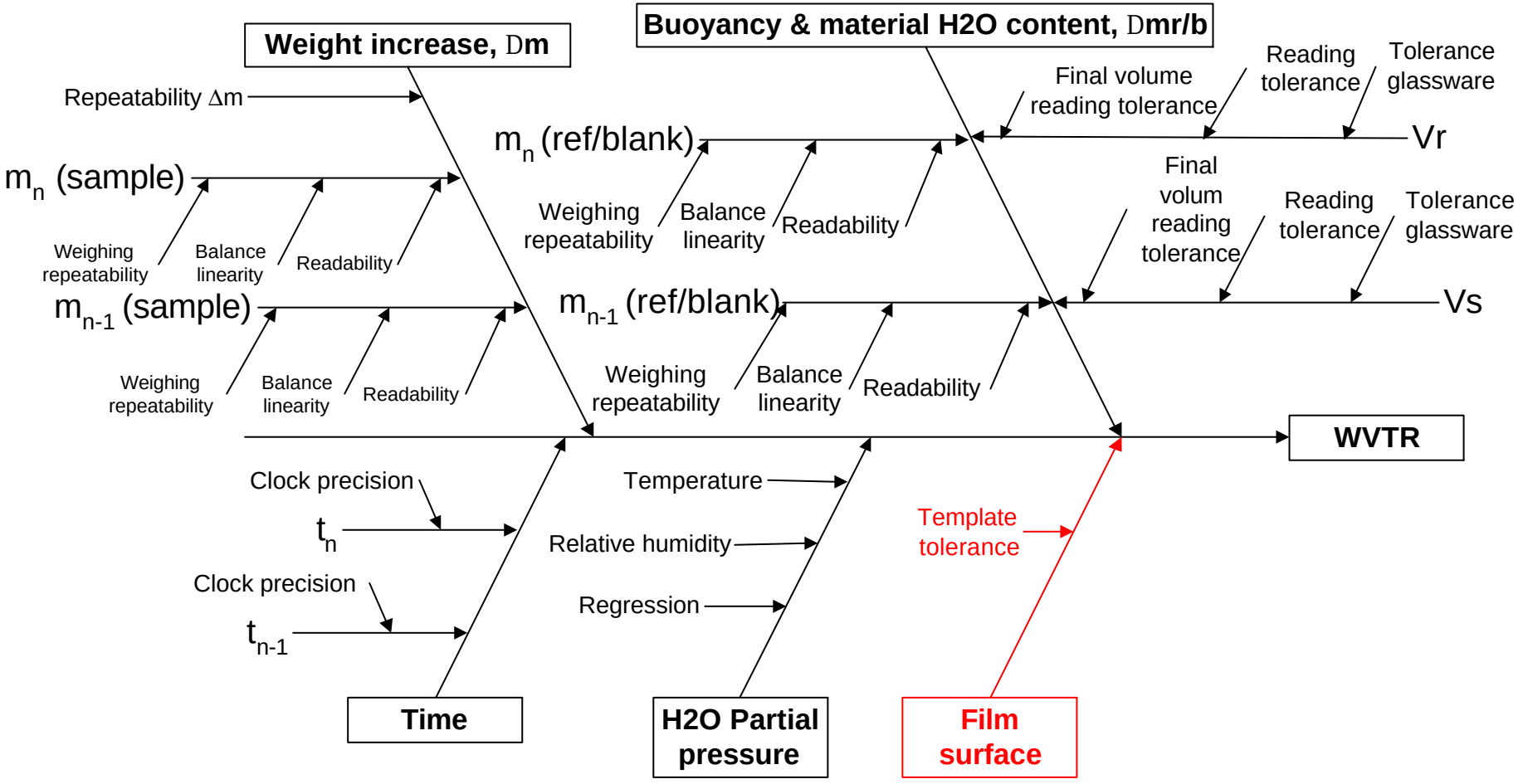
Weighing, t_n

WVTR Expression

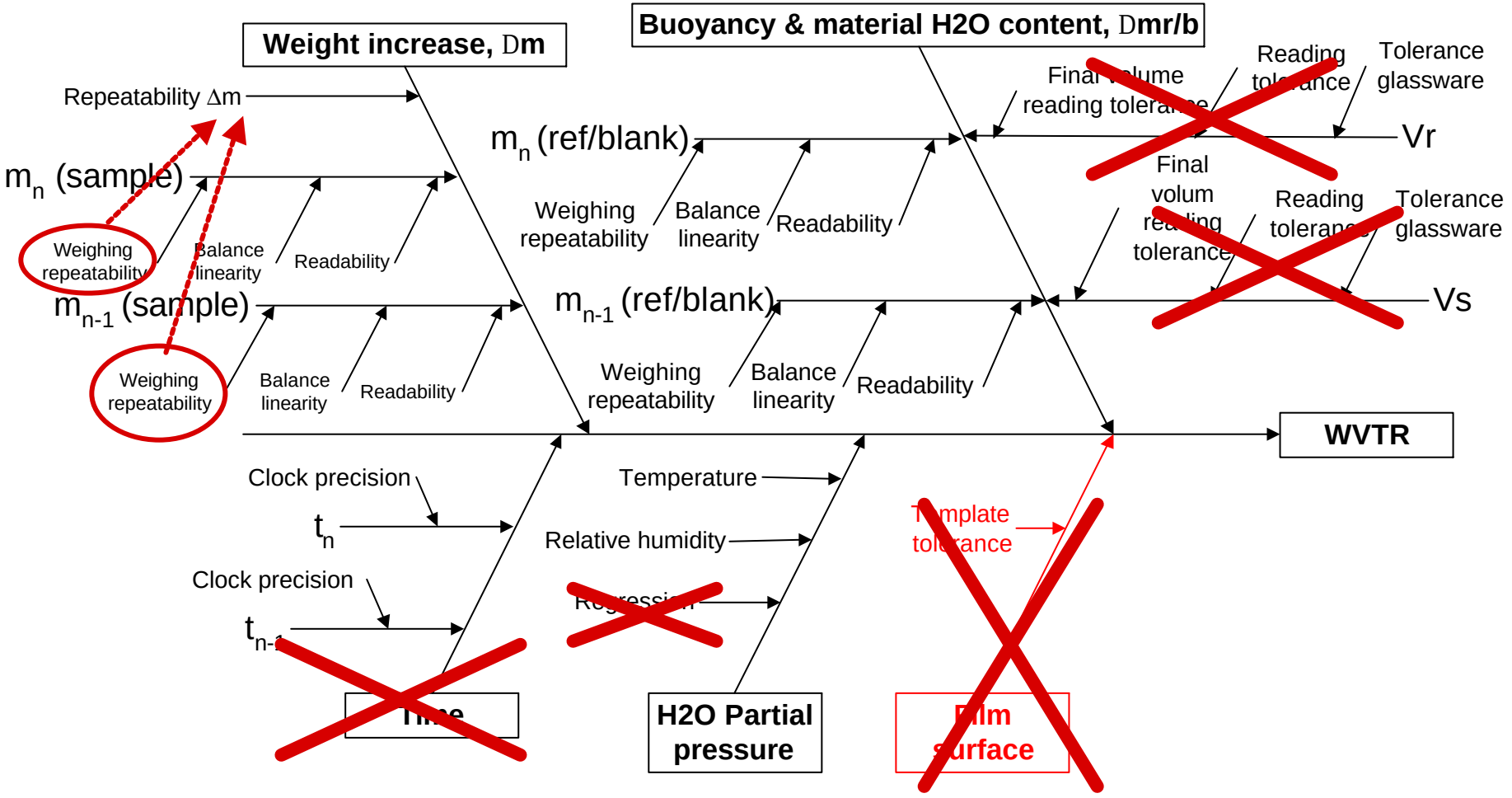
Method	Rigid container [mg/pack.day] Flexible film [g/m^2.day]
Weight gain with blank	$WVTR = \frac{(m_n - m_{n-1}) - (m_n^b - m_{n-1}^b)}{A(t_n - t_{n-1})}$
Weight gain with reference volume	$WVTR = \frac{(m_n - m_{n-1}) + (m_n^r - m_{n-1}^r)(V_s / V_r)}{(t_n - t_{n-1})}$

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]

Cause & Effect Diagram



Refined Cause & Effect Diagram



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

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

Sample (average of several specimens)

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

Reference/blank (one specimen)

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

H_2O Partial pressure

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

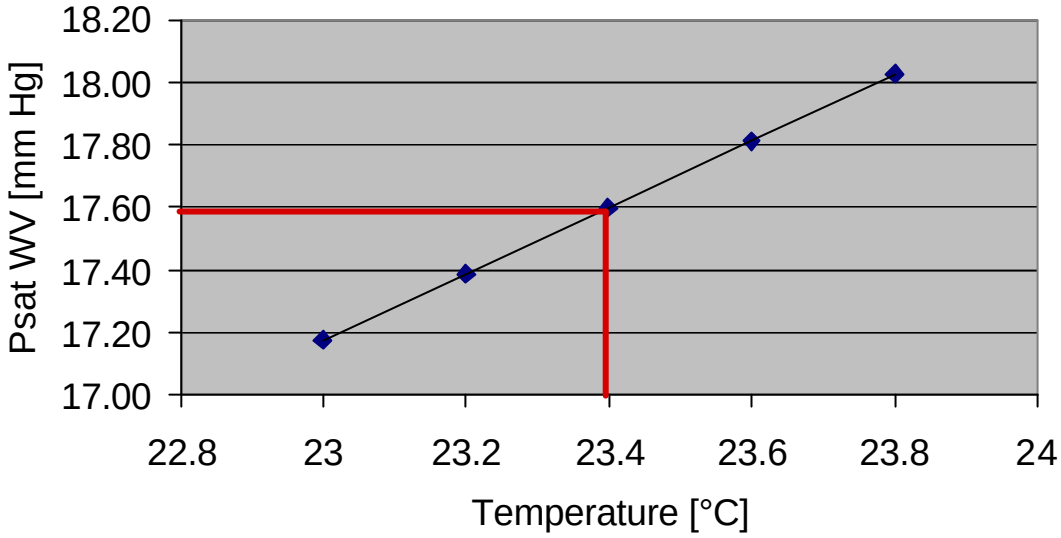
$P_{int} = 0$

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

$T = 23.4 \pm 0.4\ °C = x_0$

$RH = 81.5 \pm 1.2\ \%RH$

$$u_{regr} = \sqrt{SD_{regr}^{\,2}\left(\frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum (x_i - \bar{x})^2}\right)}$$



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

Good Food, Good Life

Met-PET

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	0.0017	0.0014	199.9421	0.074	0.47
Δmb/dt	-0.0006	0.0015	-199.942	0.085	0.53
A	0.005	0.00001	-92.2913	0.000	0.00
P H2O	1	0.02	0.46	0.000	0.00
Total (ciuj)^2				**0.160**	**1.00**
Total (ciuj) [g/m2.day]	**0.46**			**0.40**	
Relative (ciuj)				**0.87**	

PET

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	0.04	0.0022	199.9421	0.2014	0.65
Δmb/dt	0.00	0.0015	-199.942	0.0851	0.27
A	0.005	0.00001	-1526.73	0.0005	0.00
P H2O	1	0.02	7.64	0.0240	0.08
Total (ciuj)^2				**0.311**	**1.00**
Total (ciuj) [g/m2.day]	**7.64**			**0.56**	
Relative (ciuj)				**0.07**	

Combined Uncertainty: Containers & Blank

Nestlé
Good Food, Good Life

Bottle (low barrier): 21.45 ± 0.98 mg/pack.day (k=2)

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	21.74	0.161	1	0.0258	0.11
Δmb/dt	0.29	0.147	-1	0.0217	0.09
P H2O	1	0.02	21.45	0.1893	0.80
Total (ciuj)^2				**0.237**	**1.00**
Total (ciuj) [mg/pack.day]	**21.45**			**0.49**	
Relative (ciuj)				**0.02**	

Jar (high barrier) 0.79 ± 0.48 mg/pack.day (k=2)

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	1.21	0.190	1	0.0363	0.62
Δmb/dt	0.43	0.147	-1	0.0217	0.37
P H2O	1	0.02	0.79	0.0003	0.00
Total (ciuj)^2				**0.058**	**1.00**
Total (ciuj) [mg/pack.day]	**0.79**			**0.24**	
Relative (ciuj)				**0.31**	

Combined Uncertainty: Containers With Reference Volume

Nestlé
Good Food, Good Life

Bottle (low barrier): 21.85 ± 0.96 mg/pack.day (k=2)

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	21.74	0.161	1	0.0258	0.11
Δmr/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) 1.32 ± 0.42 mg/pack.day (k=2)

Source	Value	uj	ci	(ujci)^2	urel
Δm/Δt	1.21	0.190	1	0.0363	0.84
Δmr/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**	

Conclusions

- Present method only suited for low to medium barrier materials
- Dominant uncertainty contribution from climate control uncertainty for low barrier containers, significant contribution for low barrier films
- Sensitivity of balance limiting factor for high barrier materials
  - Prolong testing period
  - Use balance with higher sensitivity
- Difference in values between blank and reference volume measurements probably due to steady state moisture content of material in container walls

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**	