MEASUREMENT DATA PROCESSING

Estimation of uncertainty of volume of a 25 mL A-class volumetric flask

Group work

A study case for the selection of instruments and number of repetitions to achieve a desired uncertainty level.

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In chemical analysis, volume is one the most common sources of uncertainty:

*"**Liquid volume measurement** is an important step in most industrial and analytical measurement operations. Volume instruments are used in many fields like chemistry, health, biology and pharmacy. In several applications within these fields the measurement of volume is **significant** or **even critical**, therefore it is important to ensure that volume quantities measured using these instruments are **reliable**."*

Euramet, Calibration Guide 19

Volumetric flasks are flat bottomed glassware with elongated necks with gauge marks. They are calibrated to the gauge mark at a specified temperature.

Two classes of accuracy are specified:

Class A for higher grade

Class B for lower grade

https://www.eiscolabs.com/products/ch1952d

The problem..

Choose the <u>instruments</u> and the <u>number of measurements</u> required to achieve the desired relative uncertainty of **0.0050%** for the volume of a 25 mL A-class volumetric flask.

Nr	Variable	Mean measured value	1. instrument Analytical balance 0.01 mg [2] Digital thermometer 0.01 °C [5]			2. instrument Analytical balance 0.1 mg [3] Digital thermometer 0.1 °C [6]			3. instrument Kitchen balance 0.1 g [4] Mercury thermometer 0.1 °C [7]		
			Resol.	Inst. Err	Stdev	Resol.	Inst. Err	Stdev	Resol.	Inst. Err	Stdev
1	m_1, g	49.8538	0.00001	0.00005	0.00020	0.0001	0.0005	0.0007	0.1	0.1	0
2	m_2, g	74.7533	0.00001	0.00005	0.00500	0.0001	0.0005	0.0050	0.1	0.1	0
3	T, °C	24	0.01	0.05	0.03	0.1	0.5	0.1	0.1	0.3	0.3

B1

B2

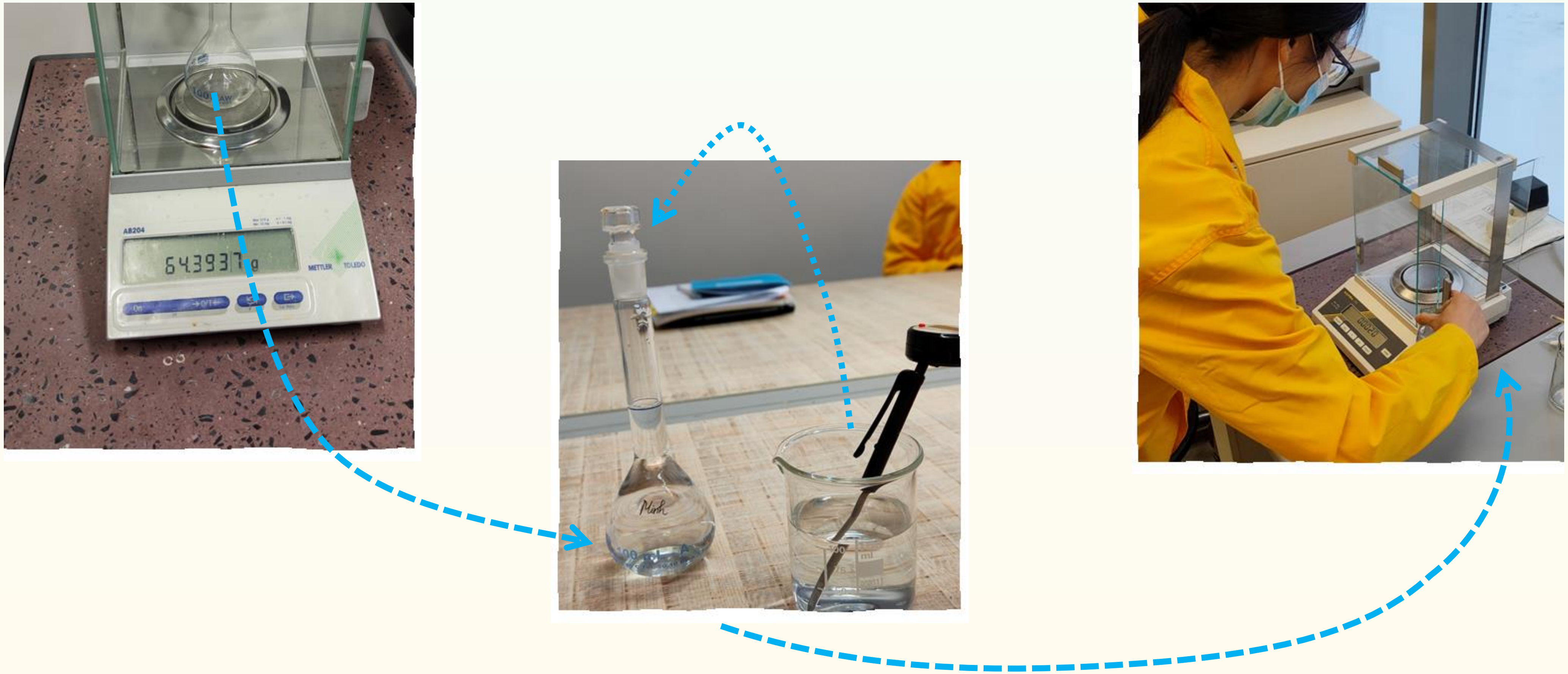
B3

T1

T2

T3

Gravimetry: a primary method



Mathematical model

$$V = \frac{m_2 - m_1}{a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4}$$

Where,

V	volume of flask, mL
m_2	mass of flask filled with water, g
m_1	mass of clean and dry flask, g
T	temperature of water, °C
a_0	9.999E-01
a_1	6.327E-05
a_2	-8.524E-06
a_3	6.943E-08
a_4	-3.821E-10

Problem-solving approach: trial & error

Reducing the number of measurement systems and testable experiments

Arrangement	m_1	m_2	T
1	B1	B1	T1
2	B1	B1	T2
3	B1	B1	T3
4	B1	B2	T1
5	B1	B2	T2
…	…	…	…
27	B3	B3	T3

Arrangement	m_1	m_2	T
1	B1	B1	T1
2	B1	B1	T2
3	B1	B1	T3
4	B2	B2	T1
5	B2	B2	T2
6	B2	B2	T3
7	B3	B3	T1
8	B3	B3	T2
9	B3	B3	T3

n_1 , n_2 , and n_T are **not** defined.

$n_1 = \mathbf{3}$, $n_T = \mathbf{2}$, $\boldsymbol{n_2} = ?$

Quantifying uncertainty sources

$$u(m_1) = \frac{s_{m_1}}{\sqrt{n_1}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}}$$

$$u(m_2) = \frac{s_{m_2}}{\sqrt{n_2}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}}$$

$$u(T) = \frac{s_T}{\sqrt{n_T}} + \frac{resolution}{\sqrt{12}} + \frac{ins.error}{\sqrt{3}}$$

Calculating the combined standard uncertainty

$$u_c^2(V) = \left(\frac{\partial V}{\partial m_1}\right)^2 u^2(m_1) + \left(\frac{\partial V}{\partial m_2}\right)^2 u^2(m_2) + \left(\frac{\partial V}{\partial T}\right)^2 u^2(T)$$

$$\frac{\partial V}{\partial m_1} = -\frac{1}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4}$$

$$\frac{\partial V}{\partial m_2} = \frac{1}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4}$$

$$\frac{\partial V}{\partial T} = \frac{(m_1 - m_2)(a_1 + 2a_2 T + 3a_3 T^2 + 4a_4 T^3)}{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4}$$

Estimating the expanded uncertainty

$$U(V) = k_{95\%, v_{eff}} \cdot u_c(V)$$

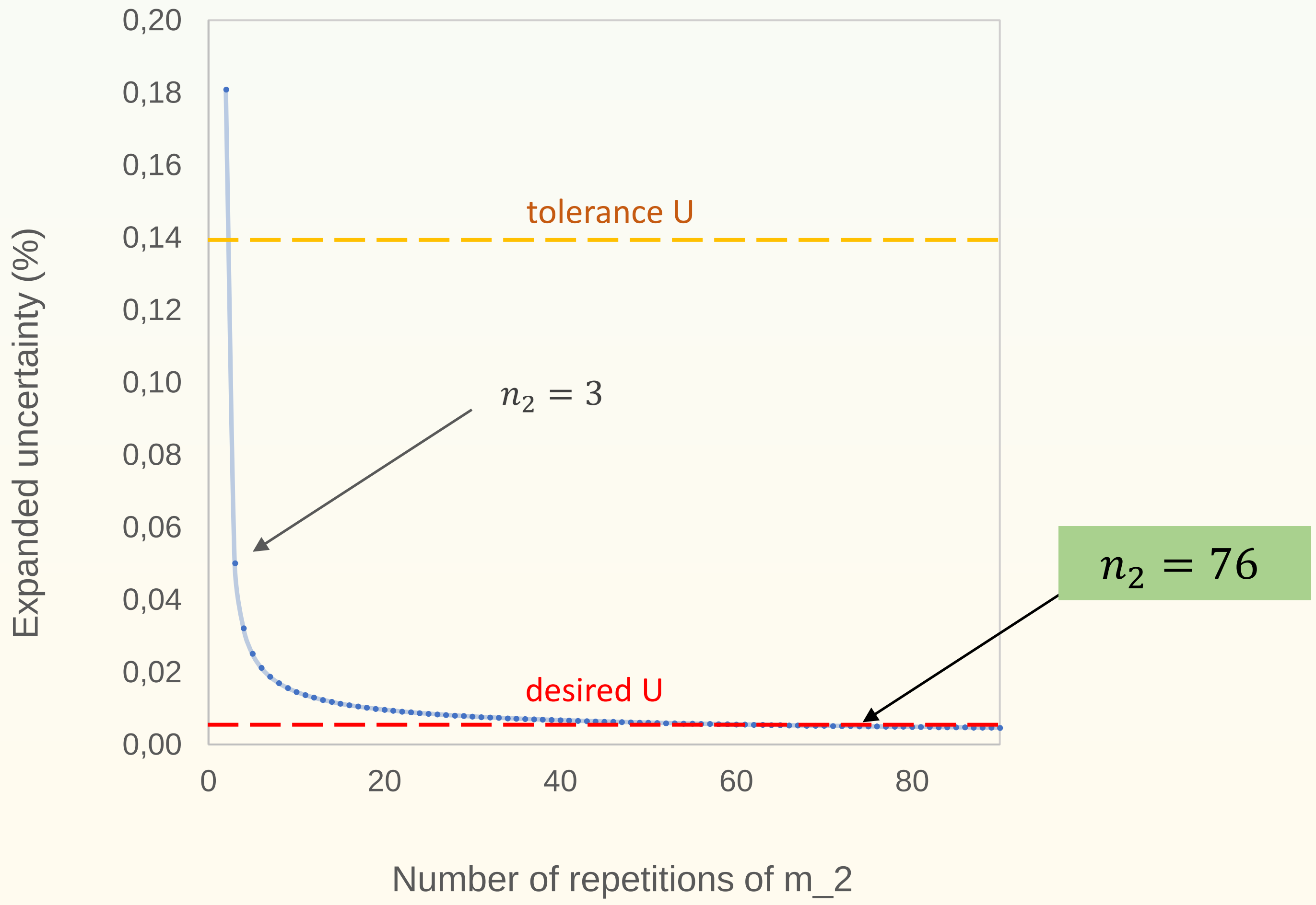
$$v_{eff}(V) = \frac{u_c^4(V)}{\frac{c_1^4 u^4(s_{m1})}{v_{m1}} + \frac{c_2^4 u^4(s_{m2})}{v_{m2}} + \frac{c_T^4 u^4(s_T)}{v_T}}$$

$$v_{m_1} = \frac{u^4(m_1)}{\frac{u^4(s_{m1})}{n_1 - 1}} \qquad v_{m_2} = \frac{u^4(m_2)}{\frac{u^4(s_{m2})}{n_2 - 1}} \qquad v_T = \frac{u^4(T)}{\frac{u^4(s_T)}{n_T - 1}}$$

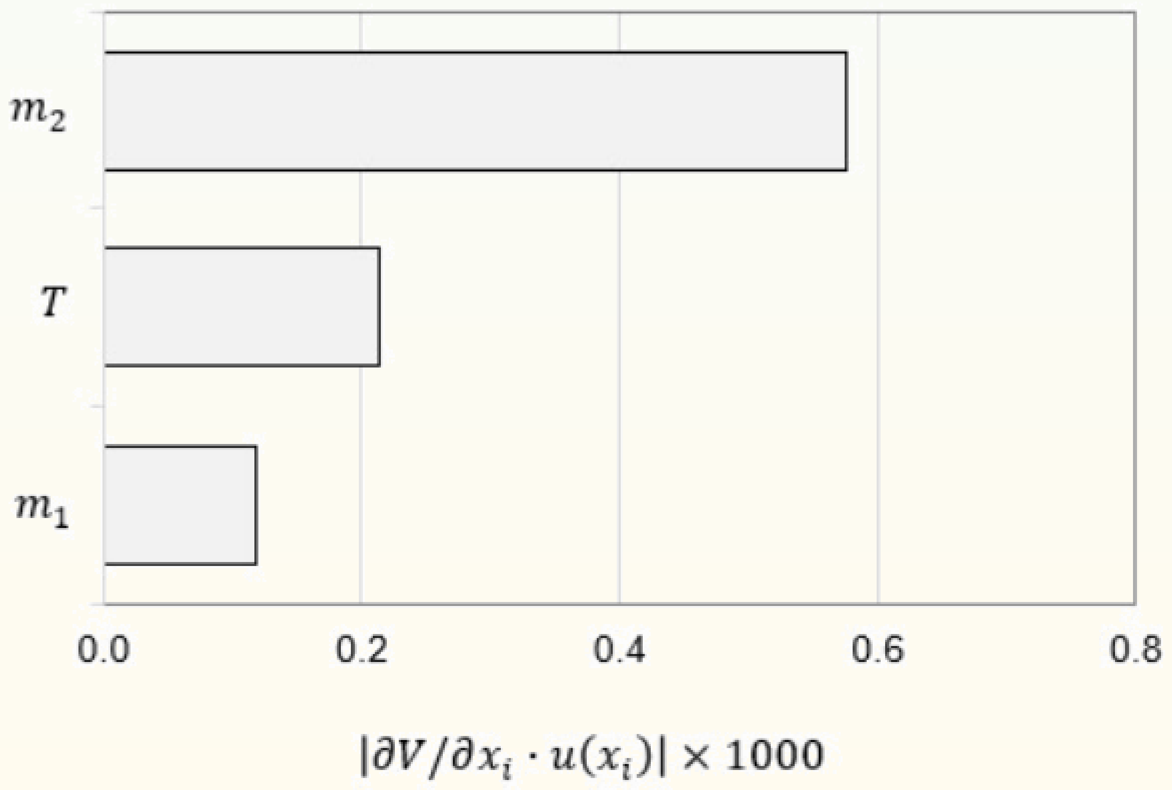
Expanded uncertainty for different sets of instruments

Set	m_1	m_2	T	n_2	$U(V), \%$
I	B1	B1	T1	3	0.0500
				76	0.0050
II	B2	B2	T2	3	0.0438
				999	0.0147
III	B3	B3	T3	999	0.7187
IV	B2	B2	T1	3	0.0508
				336	0.0050
V	B3	B3	T1	999	0.7186

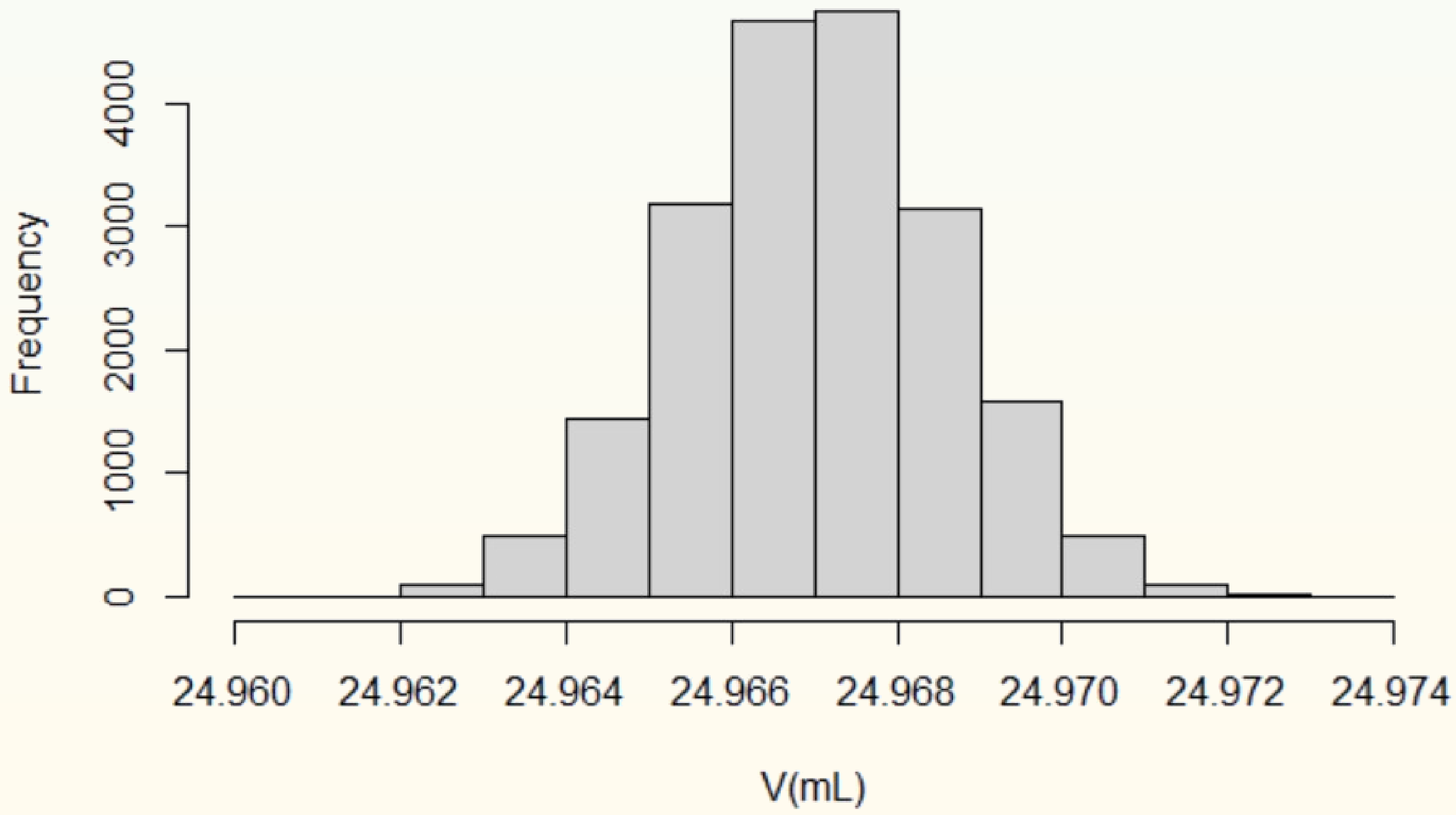
Expanded uncertainty and number of repetitions, Set I



Uncertainty contributions for Set I



Distribution of simulated values



U (V) = 0.0050%

This uncertainty coincides with the GUM result.

4. Conclusions

Set I (B1 & T1) is the best option to measure the volume of a 25 mL flask with the desired uncertainty (k95%,veff) of **0.005%**. The minimum number of repetitions is 76.

Sets I, II, and **IV** comply with the referential uncertainty of **0.14%** from tolerance. The minimum number of repetitions is 3.

Sets III and **V** are not suitable for volume calibration due to the high uncertainty contribution of the **B3** balance.

Monte Carlo simulation method shows a **similar result** compared with the GUM approach.

References

[1] ISO 1042. Laboratory glassware — one-mark volumetric flasks. 2019.

[2] ASTM E288 − 10. Standard specification for laboratory glass volumetric flasks. 2010.

[3] UKAS. Laboratory 15 - traceability: Volumetric apparatus. 2019.

[4] JCGM. Evaluation of measurement data — guide to the expression of uncertainty in measurement. 2008.

[5] Frank Jones and Georgia Harris. Its-90 density of water formulation for volumetric standards calibration. Journal of Research of the National Institute of Standards and Technology, 97:335, 05 1992.

Thanks for your attention!

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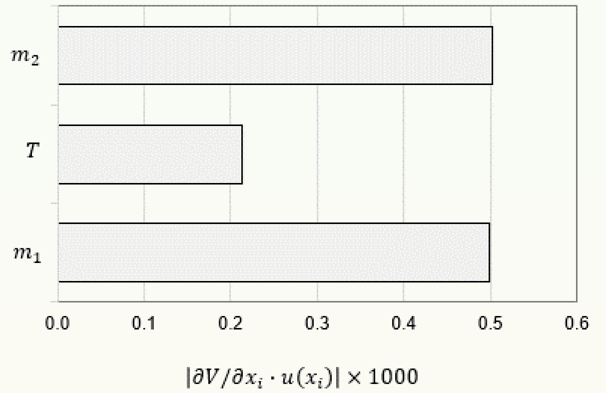
Annex: Arrangements

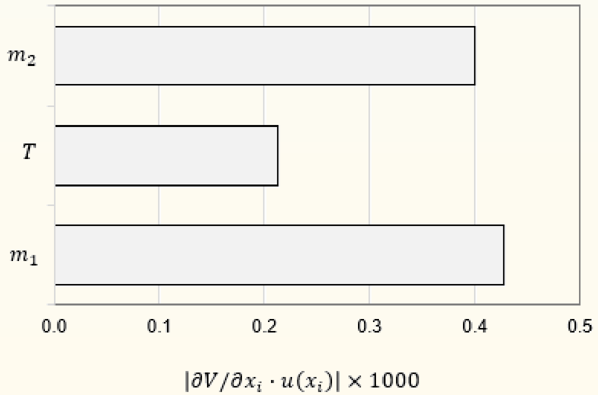
No.	$m_{\mathbf{1}}$	m_2	T	n_2	$U(V), \%$
1	B1	B1	T1	3	0.0500
2	B1	B1	T2	999	0.0140
3	B1	B1	T3	999	0.0280
4	B2	B2	T1	336	0.0050
5	B2	B2	T2	999	0.0147
6	B2	B2	T3	999	0.0222
7	B3	B3	T1	999	0.7186
8	B3	B3	T2	999	0.7187
9	B3	B3	T3	999	0.7187

Annex: Optimization

Set	m_1	m_2	T	n_2	$U(V), \%$
I	B1	B1	T1	3	0.0500
				76	0.0050
II	B2	B2	T2	3	0.0438
				999	0.0147
III	B3	B3	T3	999	0.7187
IV	B2	B2	T1	3	0.0508
				336	0.0050
V	B3	B3	T1	999	0.7186



$n_1 = 3$
$n_2 = 150$



$n_1 = 5$
$n_2 = 336$