

Standard addition

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Agenda

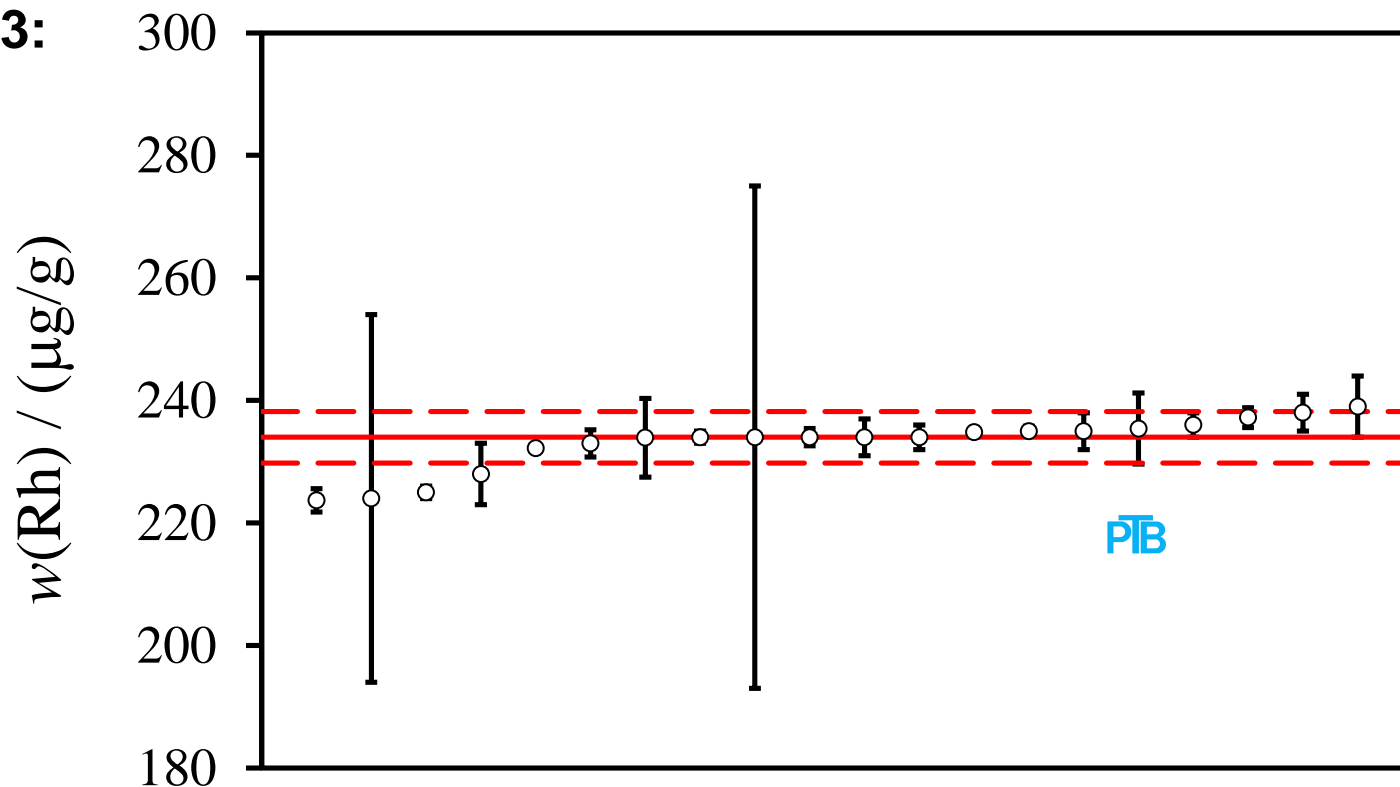
- I. principle of standard addition
- II. volumetric or gravimetric sample preparation
- III. including the mass fraction of the standard into the model equation
- IV. using an internal standard
- V. using a *natural* internal standard

I) Example: Rh in automobile catalysts

One-point calibration: $w = 450 \mu\text{g/g}$

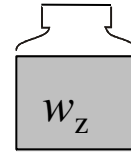
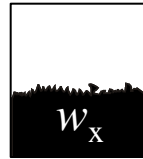
Standard addition: $w = 235.4 \mu\text{g/g}$, $u(y) = 5.8 \mu\text{g/g}$

CCQM-P63:



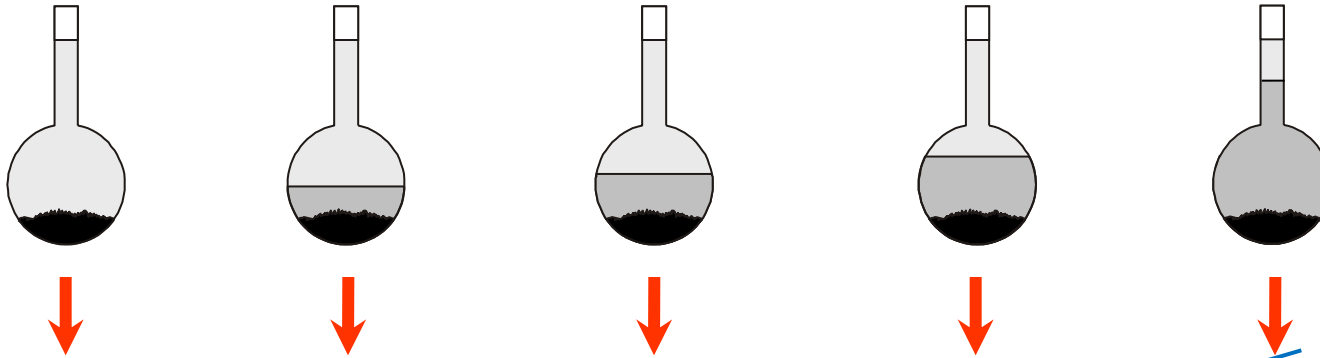
I) Principle of standard addition

Sample X
 $w_X = ?$



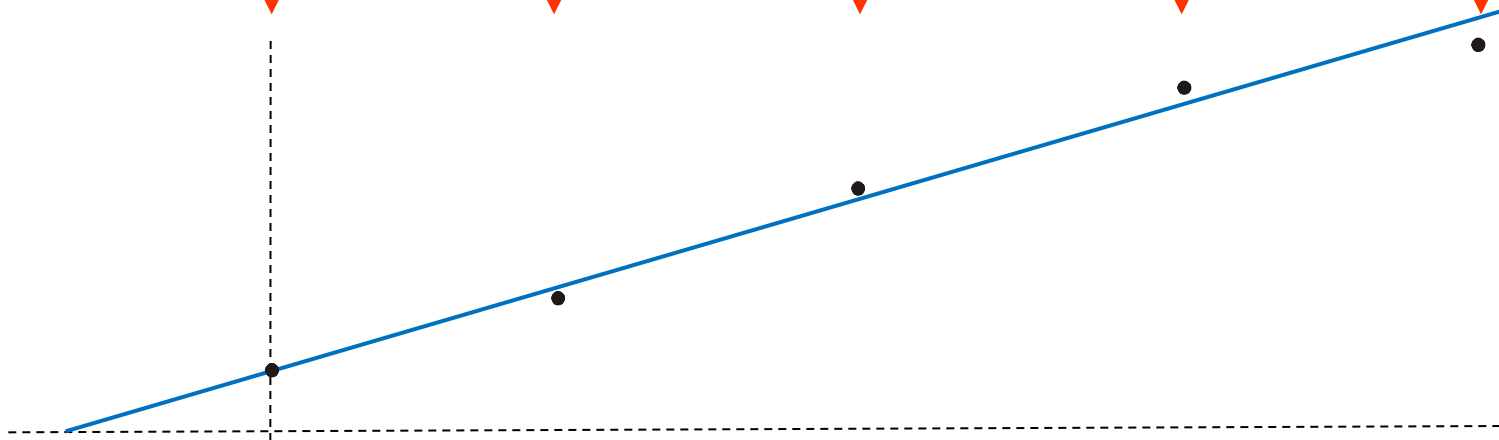
Standard Z
 w_Z known

Step 1:
Sample
preparation



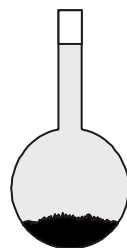
Step 2:
Measurement

Step 3:
Evaluation

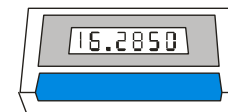
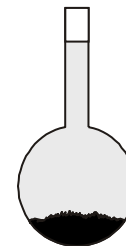


$\sim w_X$ measurand

II) Volumetric vs gravimetric preparation



VS



Volumetric preparation – common practise



DIN 32633: 1998-12: *Chemische Analytik – Verfahren der Standardaddition Verfahren, Auswertung.*



Harris, D.C.: *Quantitative chemical analysis.* New York: W.H. Freeman and Company 1998.

II) Volumetric vs gravimetric preparation

Standard addition		$y = a_1 \cdot x + a_0$	
Volumetric (DIN 32633:1998-12)	$y_i = A_i$	$x_i = \frac{V_{z,i} \cdot \beta_z}{V}$	$w_x = \frac{a_0}{a_1} \cdot \frac{V}{m_x}$
Gravimetric (DIN 32633:2013-05)	$y_i = A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i}$	$x_i = \frac{m_{z,i}}{m_{x,i}}$	$w_x = \frac{a_0}{a_1} w_z$

Disadvantages/problems of the old (volumetric) evaluation:

- Sample mass m_x or sample volume V_x 'exactly' equal in all measurement solutions
- Volume V 'exactly' equal in all measurement solutions
- Dependent on temperature

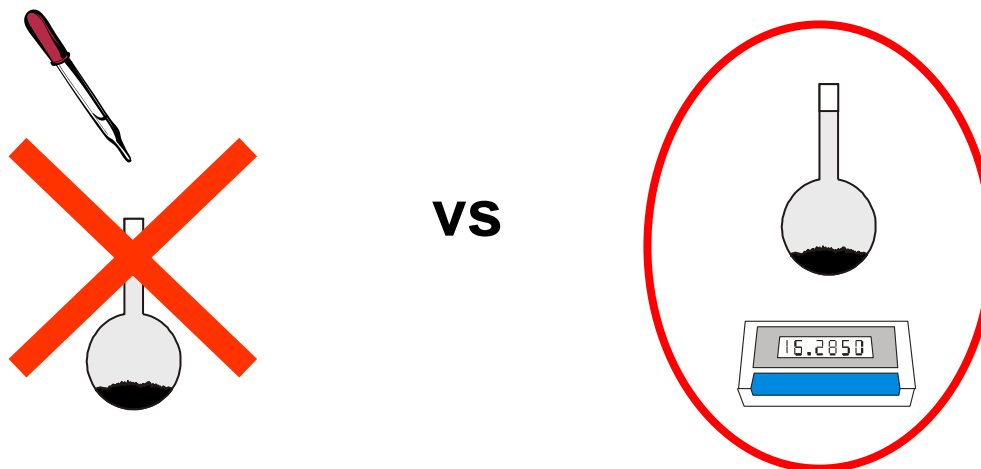
II) Volumetric vs gravimetric preparation

Therefore, in 2006 the gravimetric approach was proposed

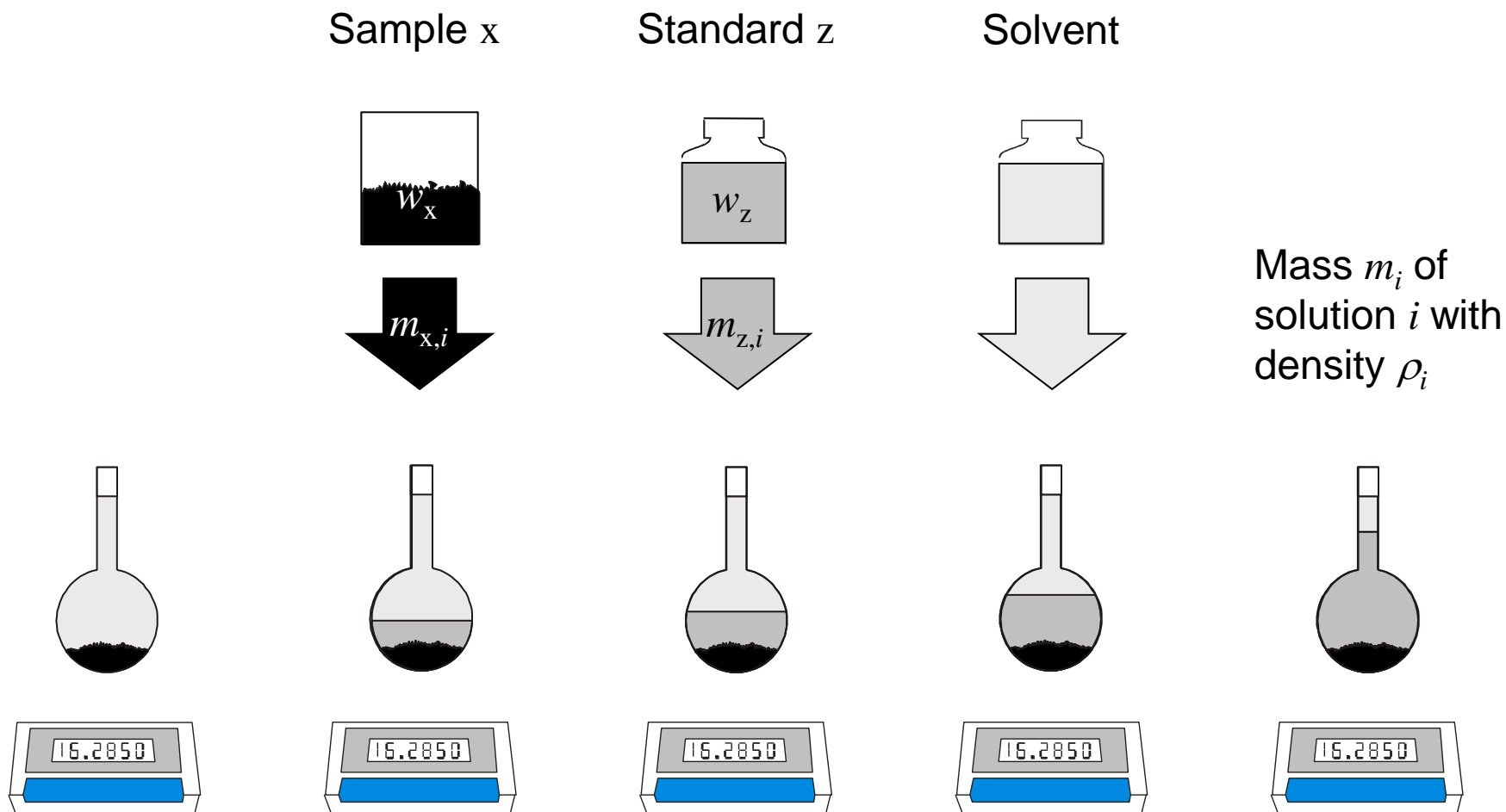
 Rienitz, O., Röhker, K., Schiel, D., Han, J., Oeter, D.: *New Equation for the Evaluation of Standard Addition Experiments Applied to Ion Chromatography*. *Microchimica Acta* 154 (2006) 21-25.

The new approach is now included in the German standard

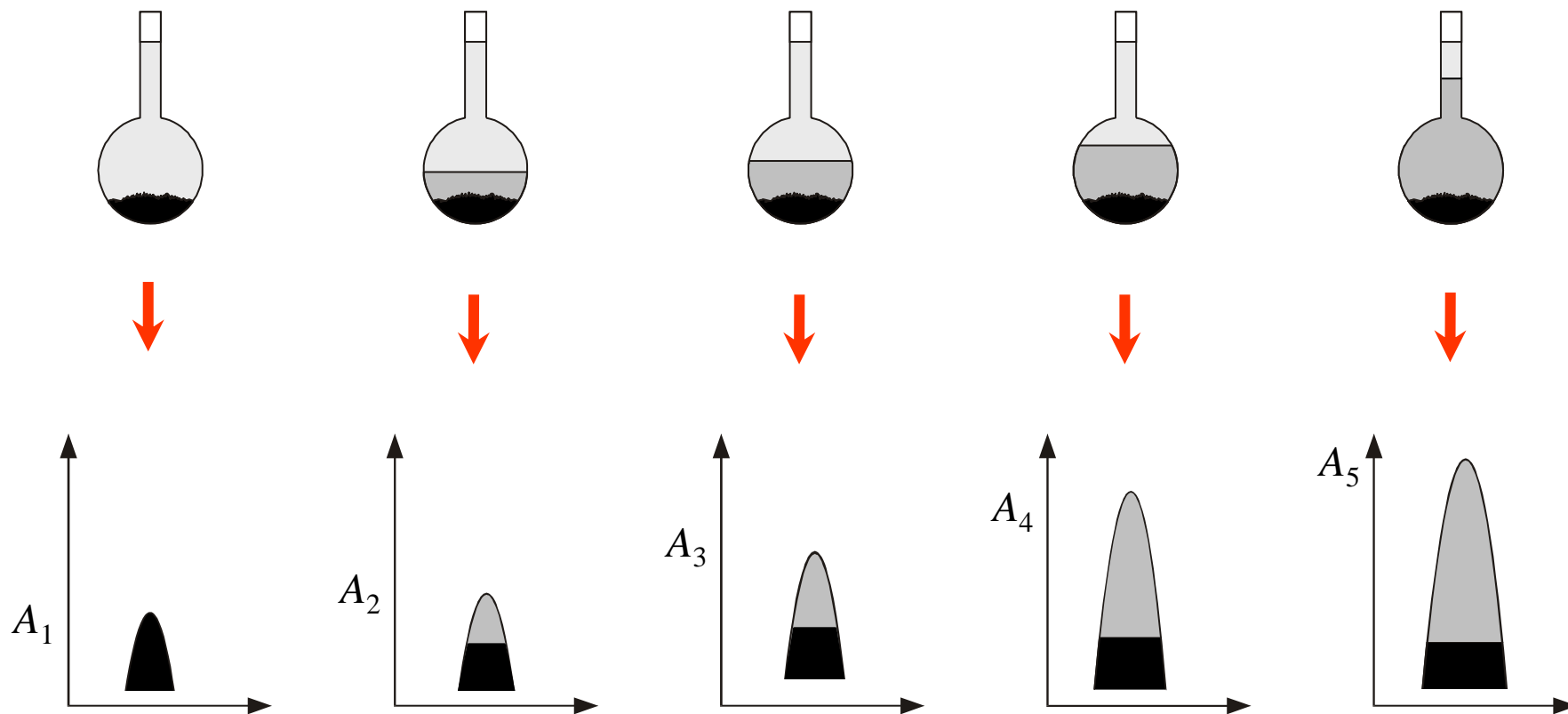
 DIN 32633: 2013-05: *Chemische Analytik – Verfahren der Standardaddition – Verfahren, Auswertung*.



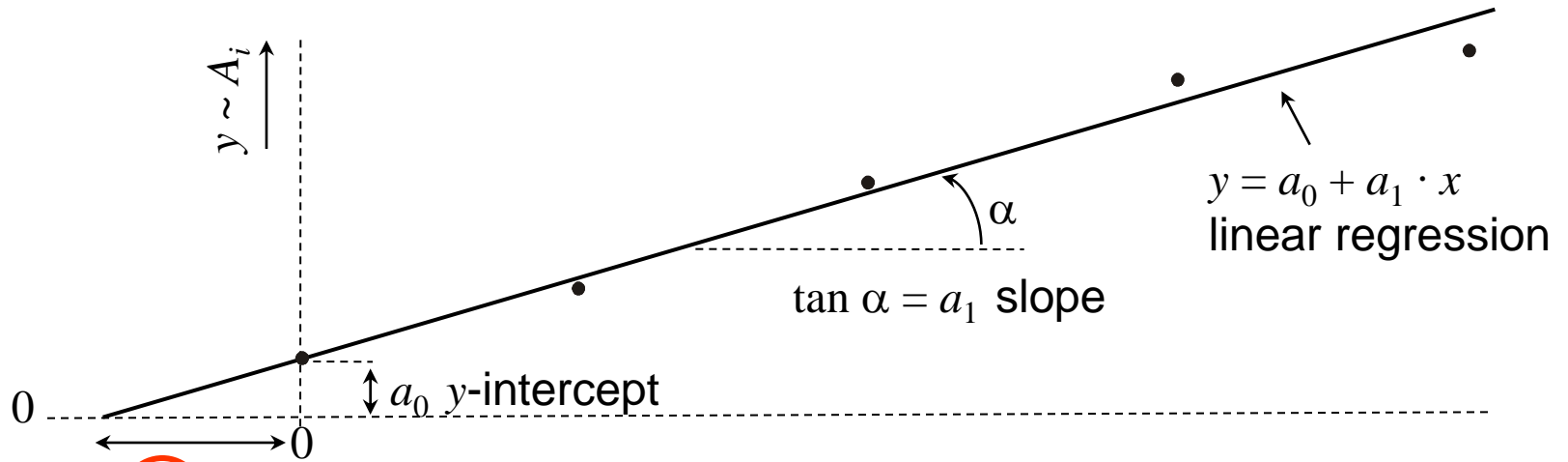
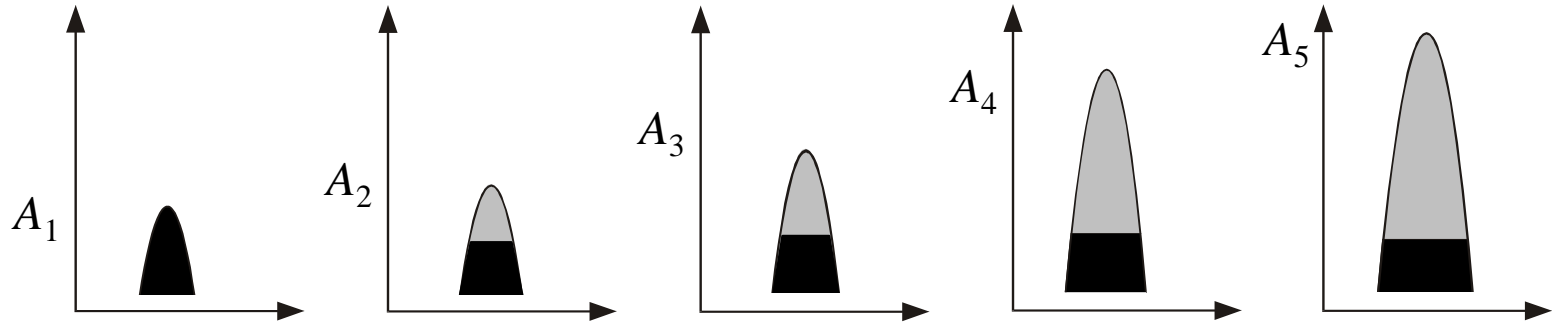
II) Step 1: Gravimetric preparation



II) Step 2: Measurement yields signal A_i



II) Step 3: Evaluation



Measurand w_x w_z ← **NEW**

$x \sim m_{z,i}$

II) Step 3: Evaluation

Linear equation:

$$A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$
$$y_i = a_0 + a_1 \cdot x_i$$

III) Including w_z

Linear equation:

$$A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$

$$y_i = a_0 + a_1 \cdot x_i$$



Including w_z in the equation for a_1 , assuming $u(a_0, a_1) = 0$

Serapinas, P., Labarraque, G., Charlet, P., Ežerinskis, Ž., Juzikiene, V.:
*Method of standard additions for arsenic measurements in water by ICP
 sector field mass spectrometry at an accuracy comparable to isotope
 dilution.* J. Anal. At. Spectrom. 25 (2010) 624-630.

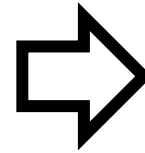


III) Including w_z

Linear equation:

$$A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$

$$y_i = a_0 + a_1 \cdot x_i$$



Model equation:



$$w_x = \frac{a_0}{a_1} \cdot w_z$$



$$a_0 = \bar{y} - a_1 \cdot \bar{x}, \quad a_1 = \frac{\sum_{i=1}^n (y_i - \bar{y})(x_i - \bar{x})}{\sum_{i=1}^n (x_i - \bar{x})^2}$$

New model equation and measurement uncertainty with $u(a_0, a_1) \neq 0$



Hauswaldt, A.-L., et al.: *Uncertainty of standard addition experiments: a novel approach to include the uncertainty associated with the standard in the model equation.* Accred. Qual. Assur. 17 (2012) No. 2, 129-138.

III) Measurement uncertainty

$$w_x = \frac{a_0}{a_1} \cdot w_z$$



Propagation of variances:

$$u_{\text{rel}}^2(w_x) = u_{\text{rel}}^2(w_z) + \frac{s_{xy}^2}{a_0^2} \cdot \left[\frac{1}{n} + \frac{\left(\frac{w_x}{w_z} + \bar{x} \right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]$$

with $\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^n x_i$ and

New: standard w_z is included

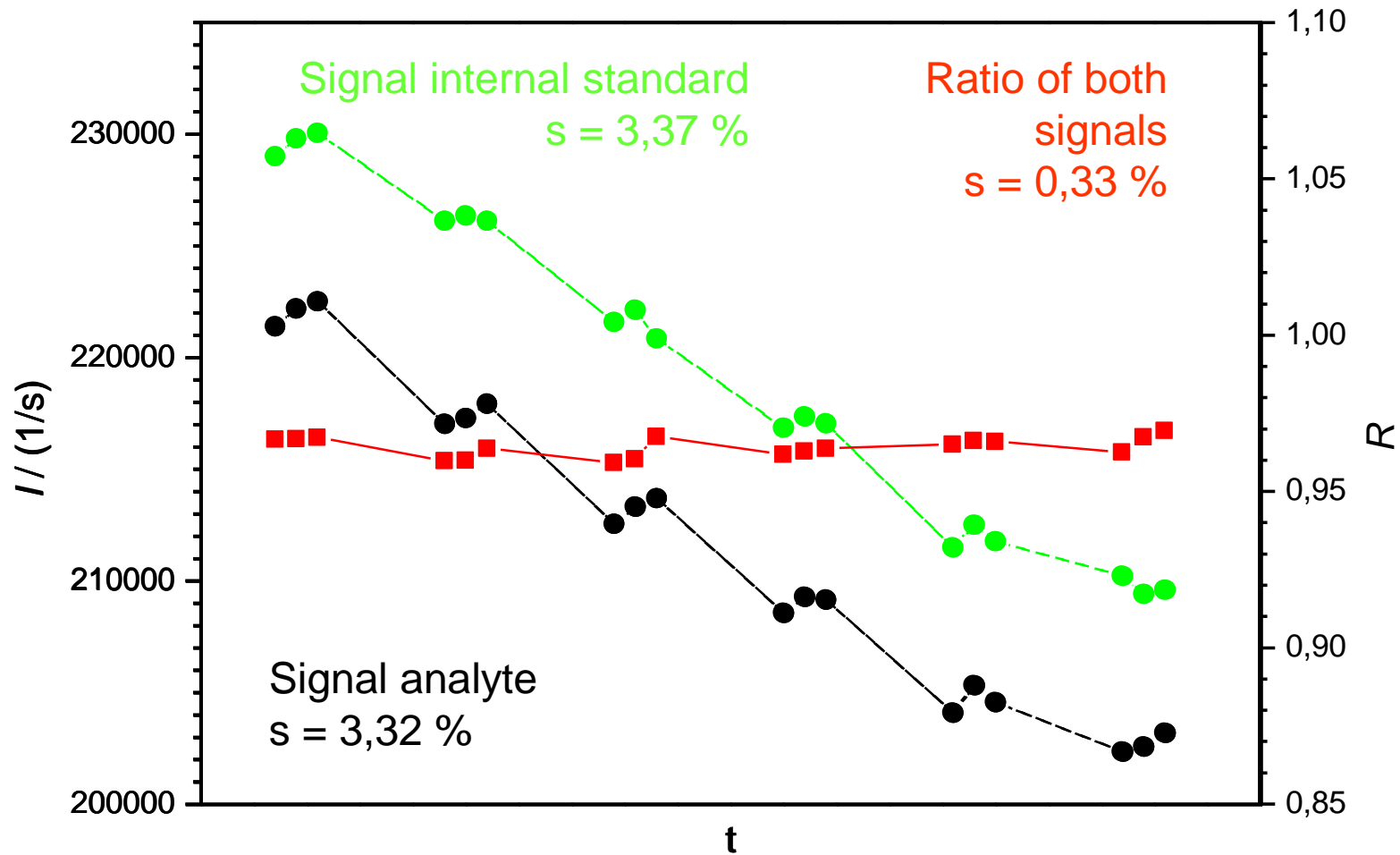
$$s_{xy}^2 = \frac{\sum_{i=1}^n [y_i - (a_0 + a_1 \cdot x_i)]^2}{n - 2}$$

Rh-example:

$$\Rightarrow w_x = 216 \mu\text{g/g}, \quad u(w_x) = 28 \mu\text{g/g} \quad \text{or} \quad u_{\text{rel}}(w_x) = 13 \%$$

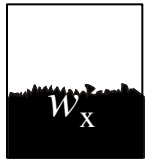
Aim: reducing the measurement uncertainty

IV) Internal standard: motivation

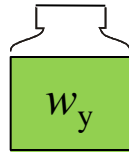


IV) Internal standard: sample preparation

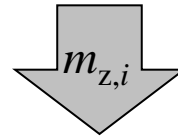
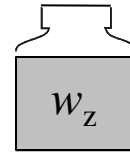
Sample x



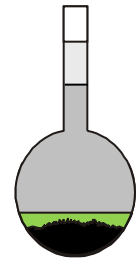
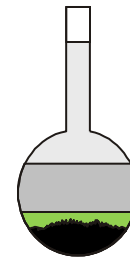
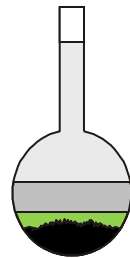
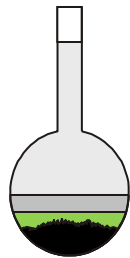
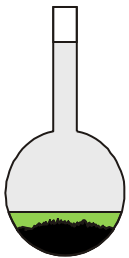
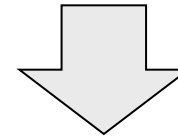
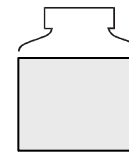
Internal
standard y



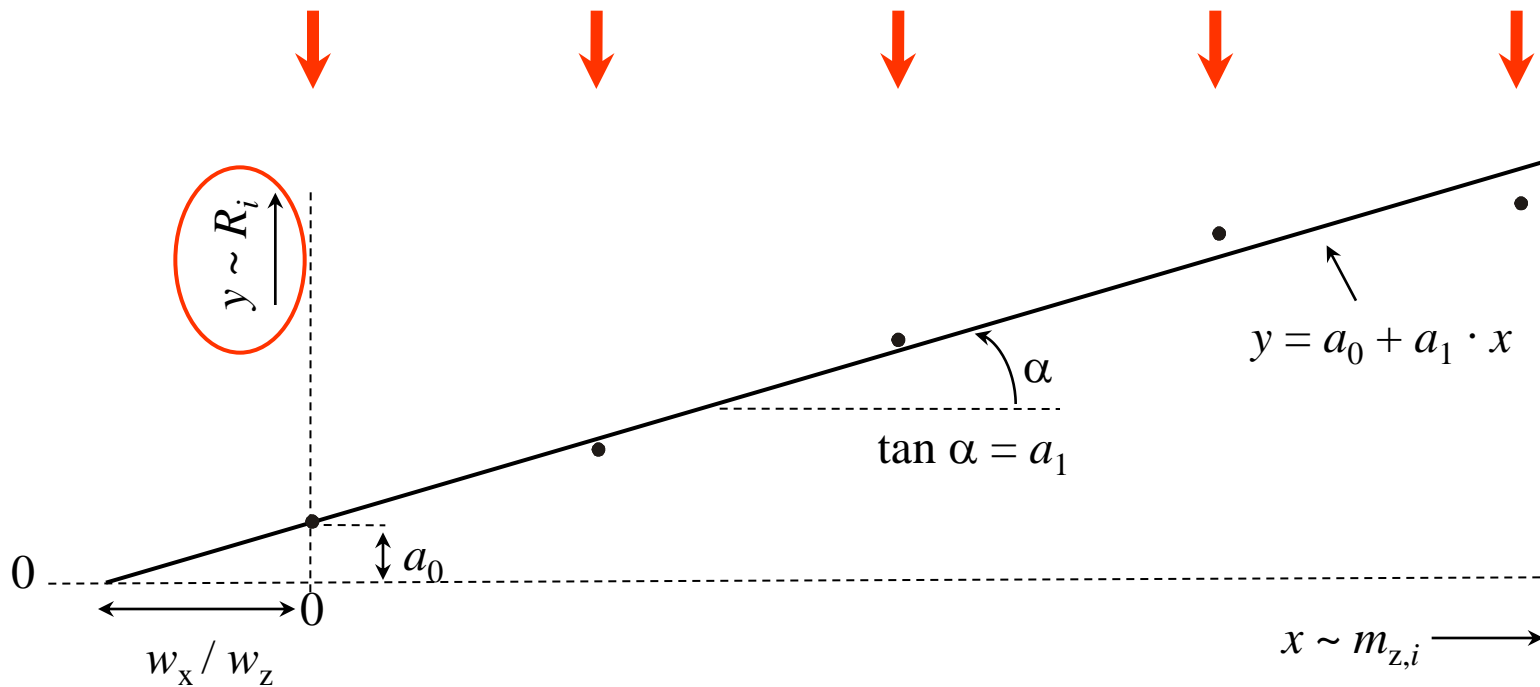
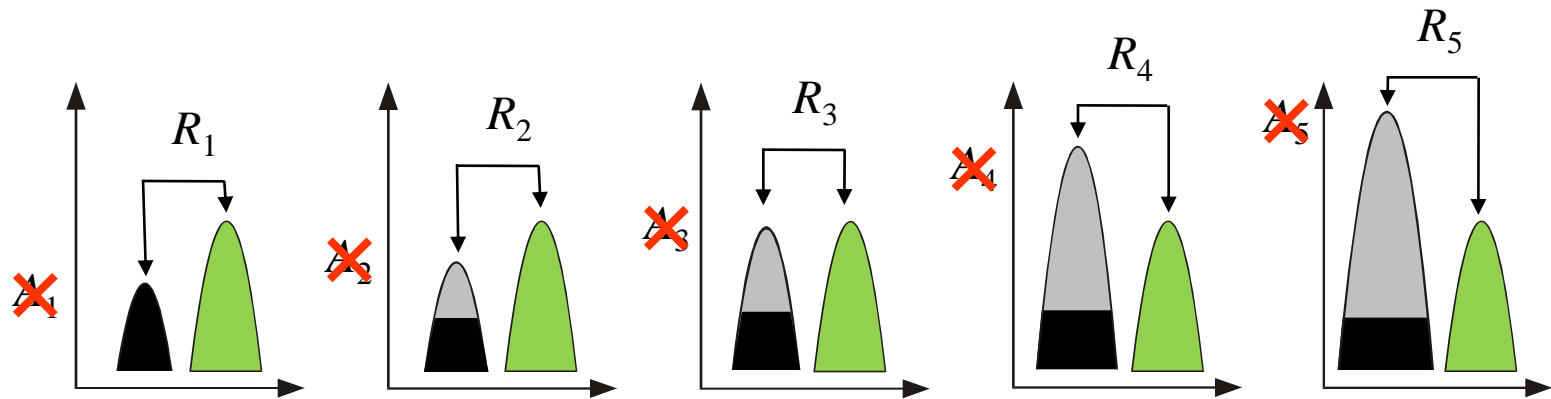
Standard z



solvent



IV) Internal standard: Ratios R_i



IV) Internal standard: equations

Linear equation:

$$R_i \cdot \frac{m_{y,i}}{m_{x,i}} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$
$$y_i = a_0 + a_1 \cdot x_i$$



Model equation:

$$w_x = \frac{a_0}{a_1} \cdot w_z$$



Measurement uncertainty:

$$u_{\text{rel}}^2(w_x) = u_{\text{rel}}^2(w_z) + \frac{s_{xy}^2}{a_0^2} \cdot \left[\frac{1}{n} + \frac{\left(\frac{w_x}{w_z} + \bar{x} \right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]$$

IV) Internal standard: equations

Linear equation:

$$R_i \cdot \frac{m_{y,i}}{m_{x,i}} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$

$$y_i = a_0 + a_1 \cdot x_i$$



Model equation:

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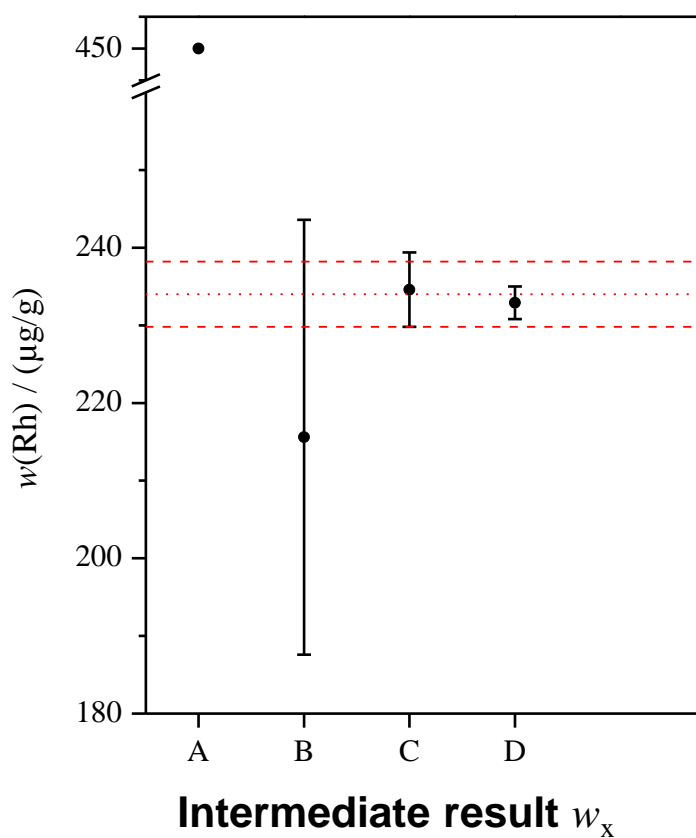
with $x_i = \frac{m_{z,i}}{m_{x,i}}$

and not $y_i = A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i}$ but $y_i = R_i \cdot \frac{m_{y,i}}{m_{x,i}}$ where $R_i = \frac{A_i(X)}{A_i(Y)}$



Standard addition with an internal standard

IV) Rh-Example: results



A) One-point calibration

Standard addition:

B) gravimetric

C) gravimetric, with internal standard

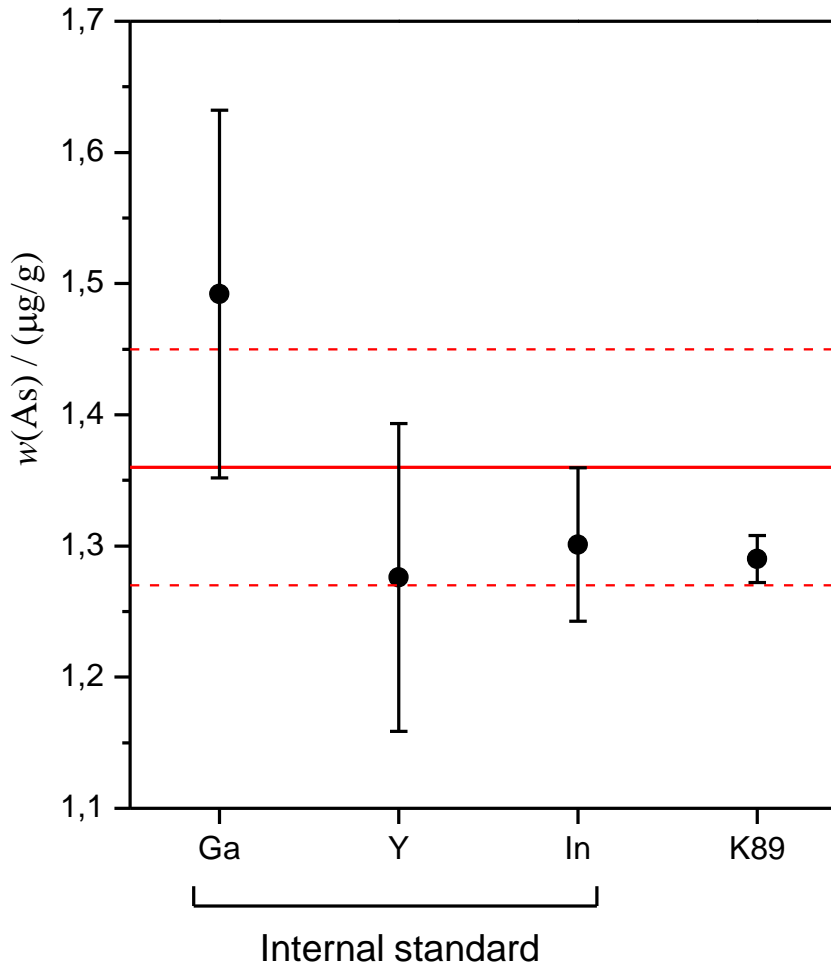
D) as C) but with a multi-collector
(MC-ICP-MS)

CCQM-P63 reference value
median with MAD_E



Rienitz, O.: *Uncertainty of standard addition experiments using an internal standard and gravimetric preparation – determination of Rh in automobile catalysts*. In: Tagungsbericht 4. VDI Fachtagung Messunsicherheit praxisgerecht bestimmen, 12./13.11.2008, Erfurt. Düsseldorf: VDI Verlag 2008, ISBN 978-3-98-12624-1-4.

V) Example: Arsenic in *Herba Ecliptae*

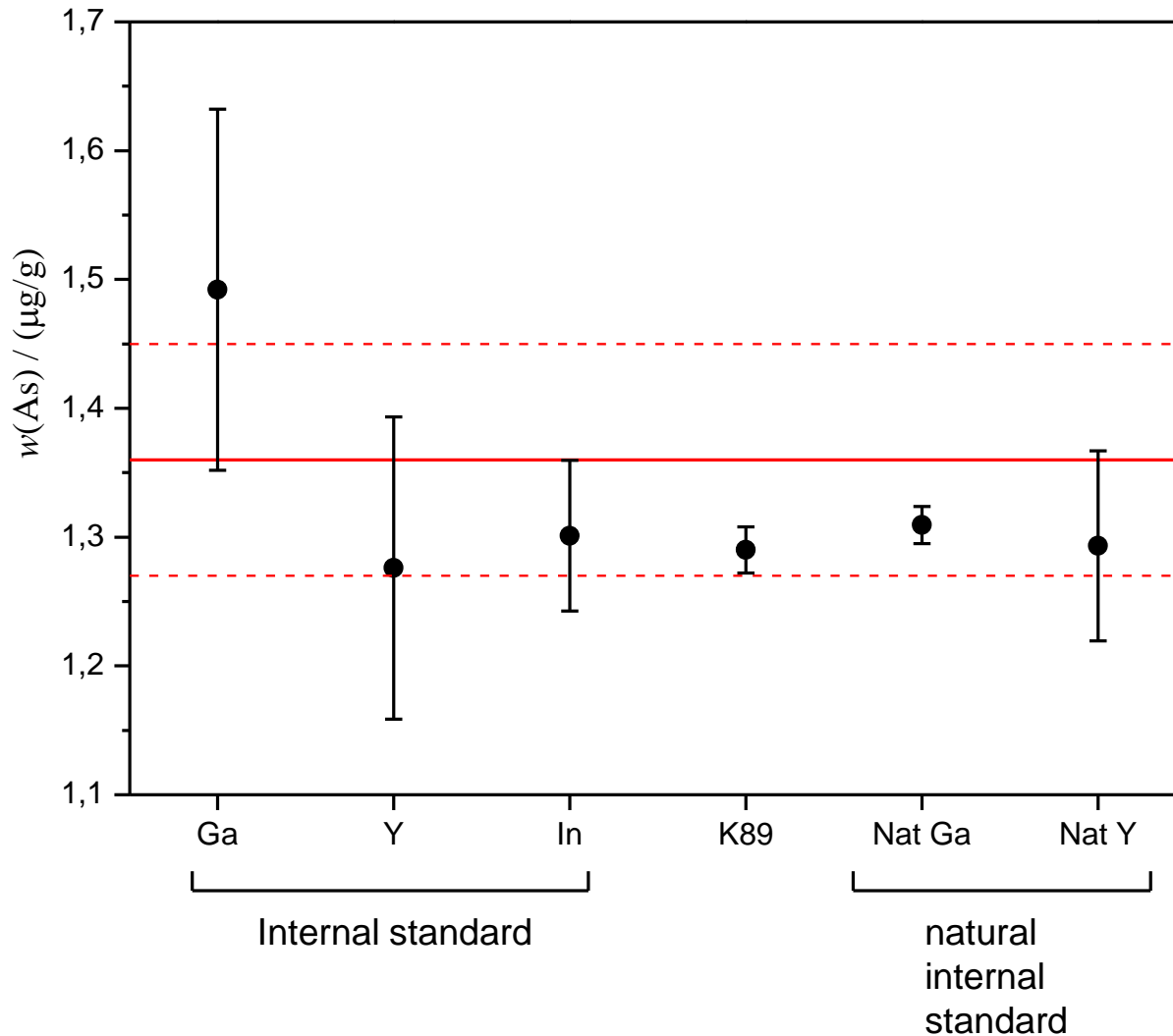


Key comparison
CCQM-K89
Measurand:
Arsenic-mass fraction

internal standard:
Gallium (^{69}Ga)
Yttrium (^{89}Y)
Indium (^{115}In)



V) Example: Arsenic in *Herba Ecliptae*

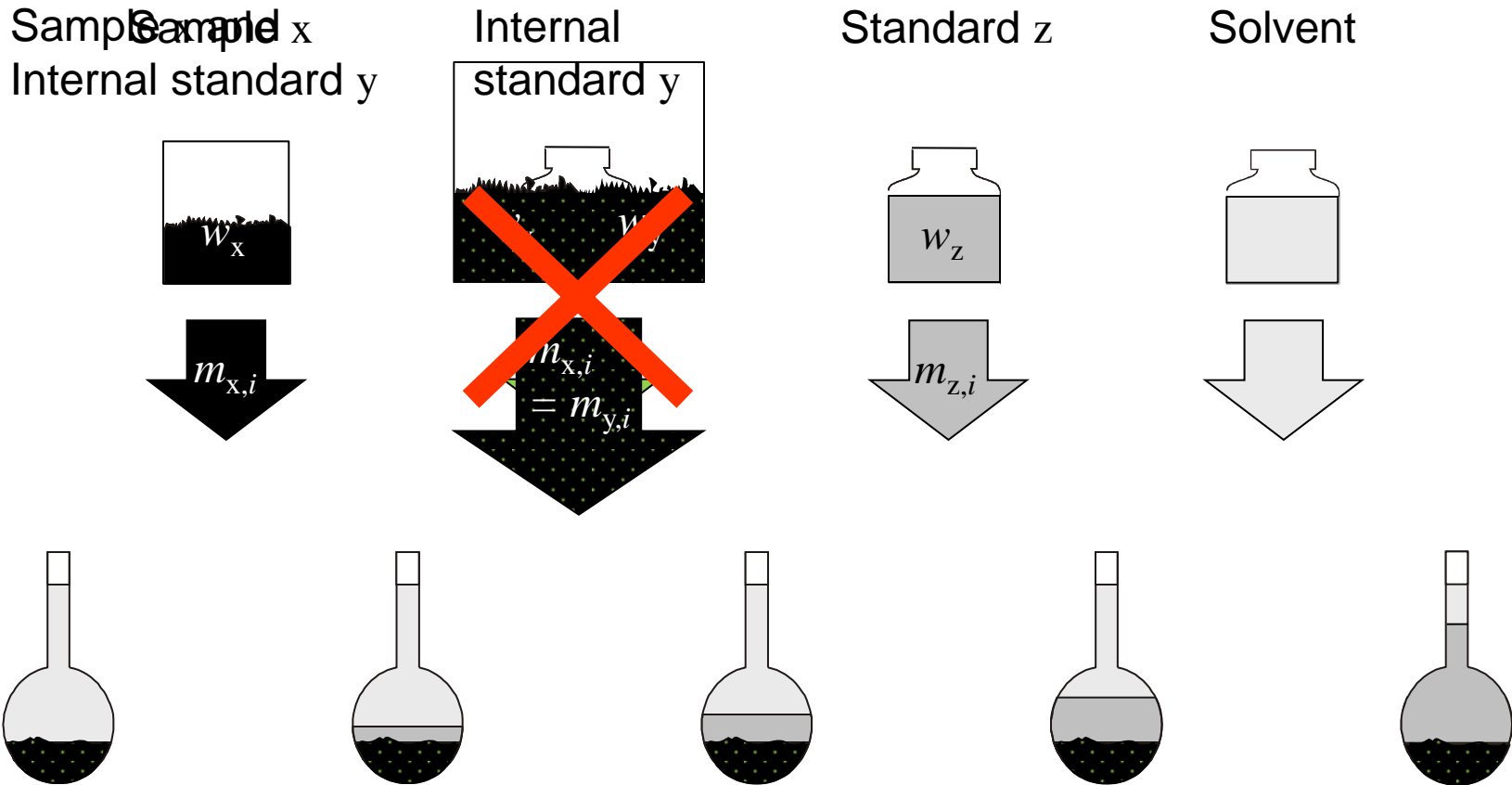


Key comparison
CCQM-K89
Measurand:
Arsenic-mass fraction

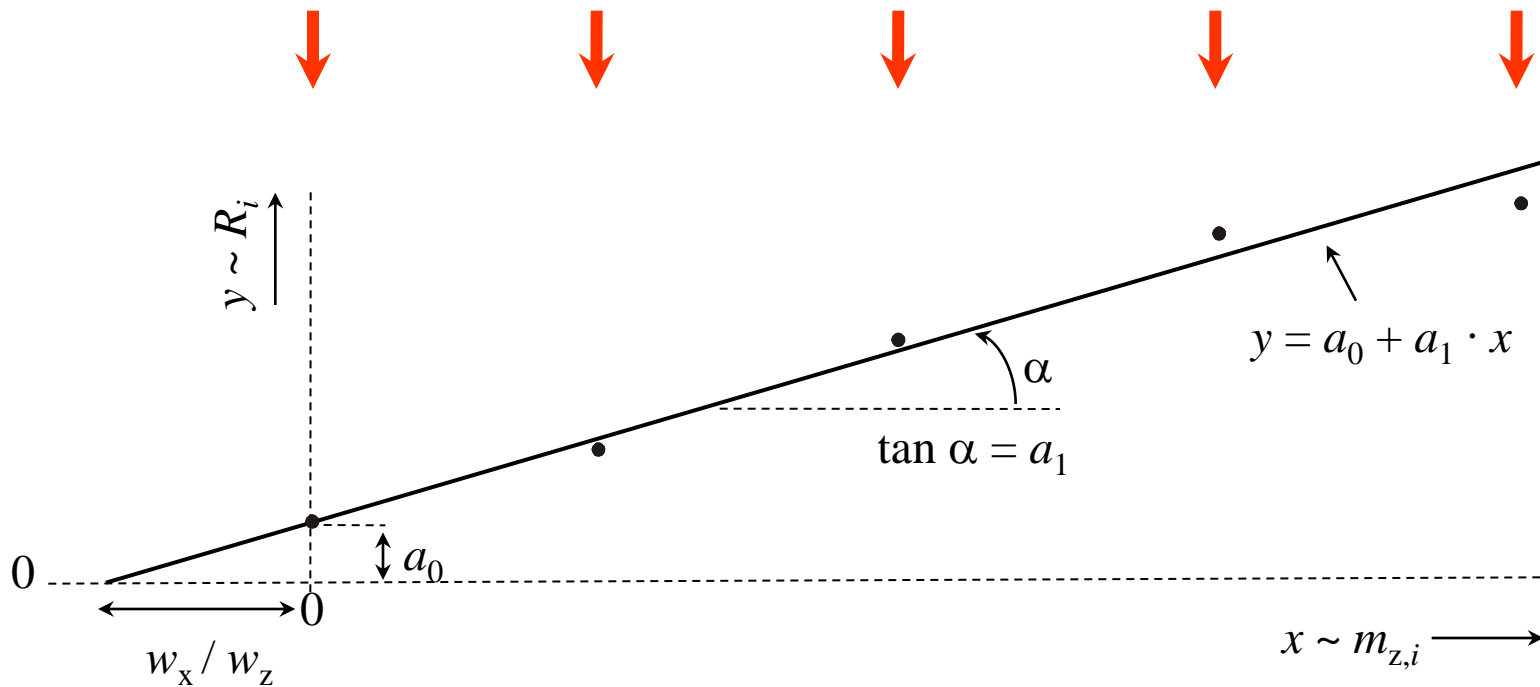
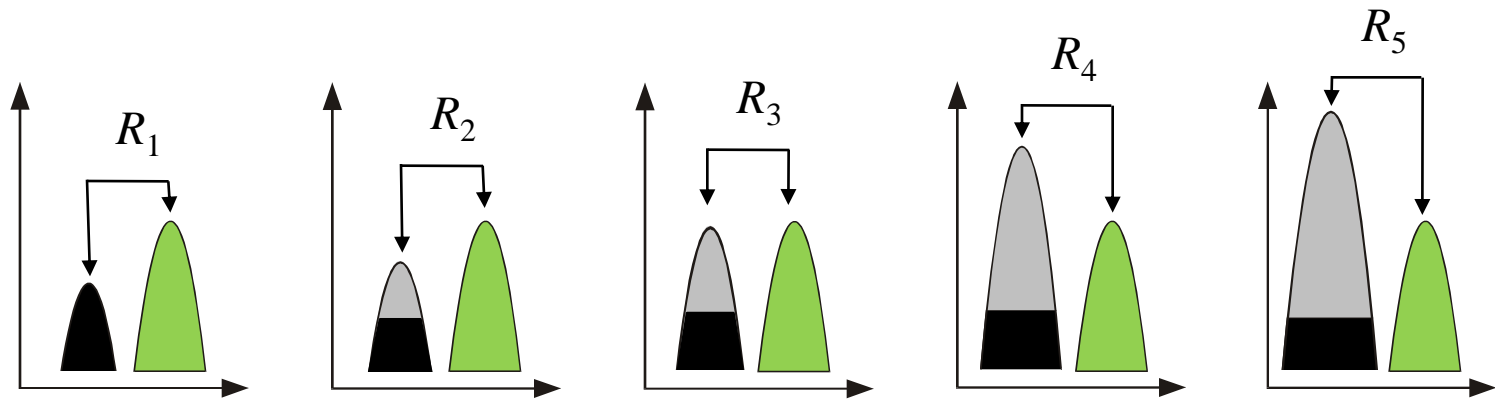
internal standard:
Gallium (^{69}Ga)
Yttrium (^{89}Y)
Indium (^{115}In)



V) Natural IS: sample preparation



V) Natural IS: measurement and evaluation



V) Overview

Linear equation:

$$R_i = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}}$$

$$y_i = a_0 + a_1 \cdot x_i$$



Model equation:

$$w_x = \frac{a_0}{a_1} \cdot w_z$$



Measurement uncertainty:

$$u_{\text{rel}}^2(w_x) = u_{\text{rel}}^2(w_z) + \frac{s_{xy}^2}{a_0^2} \cdot \left[\frac{1}{n} + \frac{\left(\frac{w_x}{w_z} + \bar{x} \right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]$$

with $x_i = \frac{m_{z,i}}{m_{x,i}}$ and

	without IS	with IS	natural IS
$y_i =$	$A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i}$	$R_i \cdot \frac{m_{y,i}}{m_{x,i}}$	R_i

as

$$m_{x,i} = m_{y,i}$$



V) Publications

Natural internal standard published in:





Hauswaldt, A.-L., Rienitz, O., Jährling, R.: *Standard addition with gravimetric preparation and internal standard – including the uncertainty associated with the internal standard – Derivation of a new model equation and use of a natural internal standard*. 135-144, in: Tagungsbericht 5. VDI Fachtagung Messunsicherheit praxisgerecht bestimmen, 8./9.11.2011, Erfurt. Düsseldorf: VDI Verlag 2011, ISBN 978-3-18-092149-5.

Rienitz, O., Jährling, R., Hauswaldt, A.-L.: *Standard addition challenge*. *Analytical and Bioanalytical Chemistry*, (2012) 403:2461-2462.

Hauswaldt, A.-L.: *Evaluation of measurement data in analytical chemistry*. PTB-Bericht CP-7. Bremerhaven: nw-Verlag 2013, ISBN 978-3-86918-308-4. (Dissertation)

DIN 32633: 2013-05: *Chemische Analytik – Verfahren der Standardaddition – Verfahren, Auswertung*.

- standard addition: elaborative and accurate
- exact model
- one straightforward equation for MU
- gravimetric sample preparation better than volumetric (2006)
-  • mass fraction w_z of the added standard z is included in the model equation (2012)
- internal standard considerably reduces the MU (2008)
-  • natural internal standard (2013)
- experiment (practical) \iff mathematics (abstract measurement)

Acknowledgements

Dr. Olaf Rienitz, Dr. Reinhard Jährling, Carola Pape,

all CITAC members for the great honor to get
the CITAC Best Papers Award 2012

Thank you for your attention!

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[1] Rienitz, O., Röhker, K., Schiel, D., Han, J., Oeter, D.: *New Equation for the Evaluation of Standard Addition Experiments Applied to Ion Chromatography*. *Microchim Acta* 154, 2006, 21-25

[2] Rienitz, O.: *Uncertainty of standard addition experiments using an internal standard and gravimetric preparation – determination of Rh in automobile catalysts*. Tagungsbericht 4. VDI Fachtagung „Messunsicherheit praxisgerecht bestimmen“, VDI Wissensforum, 2008

[3] Hauswaldt, A.-L., Rienitz, O., Jährling, R., Fischer, N., Schiel, D., Labarraque, G., Magnusson, B.: *Uncertainty of standard addition experiments: a novel approach to include the uncertainty associated with the standard in the model equation*. *Accred Qual Assur* 17, 2012, Nr. 2, 129-138

[4] Hauswaldt, A.-L., Rienitz, O., Jährling, R.: *Standard addition with gravimetric preparation and internal standard – including the uncertainty associated with the internal standard – Derivation of a new model equation and use of a natural internal standard*. 135-144, in: Tagungsbericht 5. VDI Fachtagung Messunsicherheit praxisgerecht bestimmen, 8./9.11.2011, Erfurt. Düsseldorf: VDI Verlag 2011, ISBN 978-3-18-092149-5.

[5] Rienitz, O., Jährling, R., Hauswaldt, A.-L.: *Standard addition challenge*. Analytical and Bioanalytical Chemistry, (2012) 403:2461-2462.

[6] Hauswaldt, A.-L.: *Evaluation of measurement data in analytical chemistry*. PTB-Bericht CP-7. Bremerhaven: nw-Verlag 2013, ISBN 978-3-86918-308-4 (Dissertation).

Guides

[GUM] Evaluation of measurement data – Guide to the Expression of Uncertainty in Measurement, JCGM 100:2008

[VIM] International vocabulary of metrology VIM – Basic and general concepts and associated terms, JCGM 200:2008

[DIN] DIN 32633-1, Chemische Analytik – Verfahren der Standardaddition – Verfahren, Auswertung, 2013

III) Derivation of the linear equation

$$A_i = a'_1 \cdot \gamma_i = \text{sensitivity} \cdot \text{concentration}$$

with $\gamma_i = \rho_i \cdot w_i = \text{density} \cdot \text{mass fraction of the analyte}$

$$\text{and } w_i = \frac{m_{x,i} \cdot w_x + m_{z,i} \cdot w_z}{m_i}$$



$$A_i = a'_1 \cdot \rho_i \cdot w_i = a'_1 \cdot \rho_i \cdot \frac{m_{x,i} \cdot w_x + m_{z,i} \cdot w_z}{m_i}$$



$$\begin{aligned} A_i \cdot \frac{m_i}{m_{x,i}} \cdot \frac{1}{\rho_i} &= a'_1 \cdot \frac{m_{x,i} \cdot w_x + m_{z,i} \cdot w_z}{m_{x,i}} = a'_1 \cdot w_x + a'_1 \cdot w_z \cdot \frac{m_{z,i}}{m_{x,i}} \\ y_i &= a_0 + a_1 \cdot x_i \end{aligned}$$

III) Rh-example: measurement result

$$\Rightarrow w_x = 216 \mu\text{g/g}, \quad u(w_x) = 28 \mu\text{g/g} \quad \text{or} \quad u_{\text{rel}}(w_x) = 13 \%$$

Then: complete budget for the measurement uncertainty

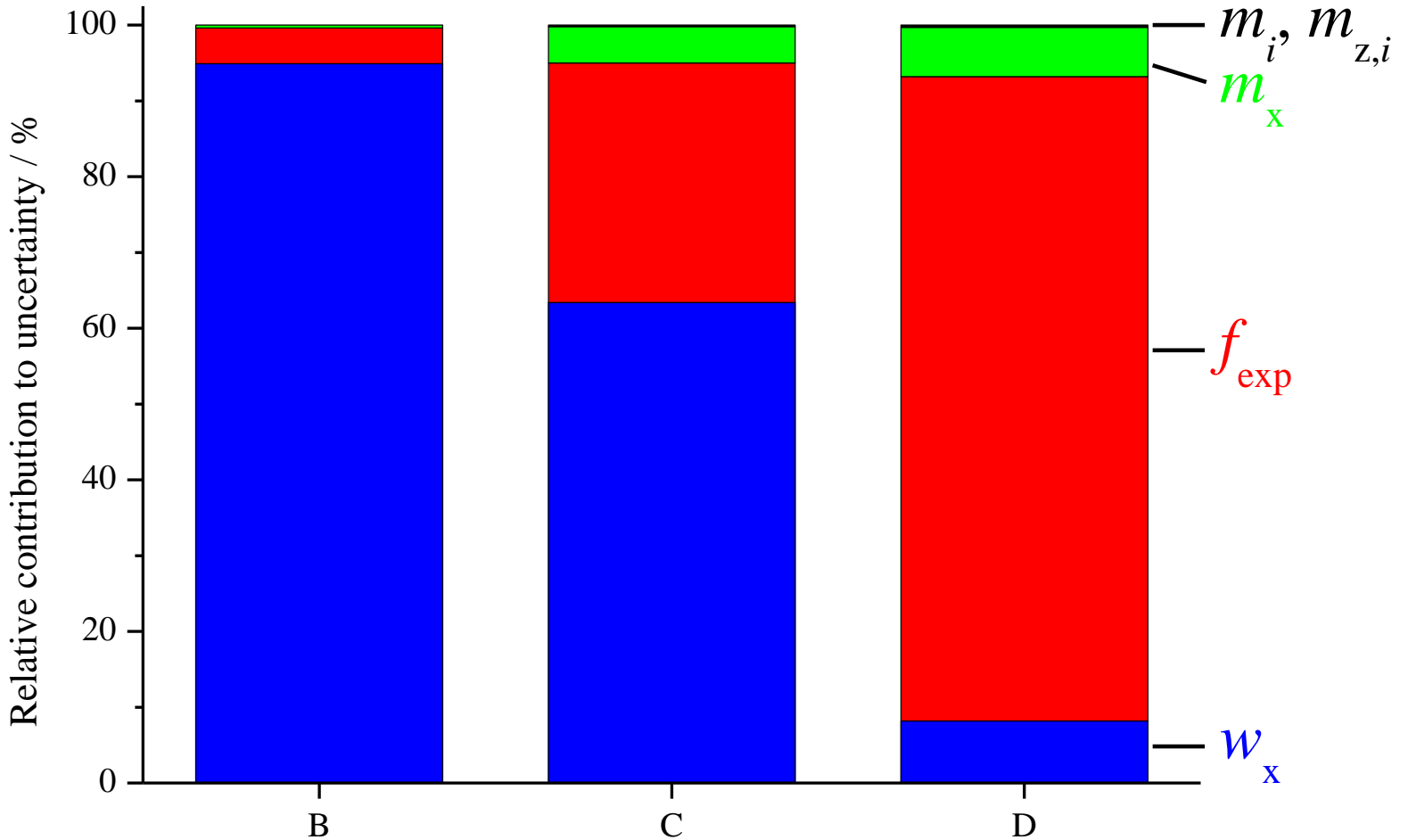
with dry mass correction, uncertainty contributions resulting from sample preparation and from the masses of sample, standard and solvent

Model equation:
$$w = \frac{1}{w_{\text{dry}}} \cdot f_{\text{exp}} \cdot w_x \cdot \delta_{\text{mx}} \cdot \delta_{\text{mz}} \cdot \delta_{\text{mi}}$$

$$\Rightarrow w = 218 \mu\text{g/g}, \quad u(w) = 29 \mu\text{g/g}$$

Aim: reducing the measurement uncertainty

III) Beispiel: Rhodium



Relative Unsicherheitsbeiträge für die Szenarien B – D

I) Messunsicherheitsberechnung

$$\begin{aligned}
 u^2(w_x) &\stackrel{\text{GUM}}{=} \left(\frac{\partial w_x}{\partial a_0}\right)^2 u^2(a_0) + \left(\frac{\partial w_x}{\partial a_1}\right)^2 u^2(a_1) + \left(\frac{\partial w_x}{\partial w_z}\right)^2 u^2(w_z) \\
 &+ 2 \cdot \left(\frac{\partial w_x}{\partial a_0}\right) \left(\frac{\partial w_x}{\partial a_1}\right) u(a_0, a_1) + 2 \cdot \left(\frac{\partial w_x}{\partial a_0}\right) \left(\frac{\partial w_x}{\partial w_z}\right) \underbrace{u(a_0, w_z)}_{=0} + 2 \cdot \left(\frac{\partial w_x}{\partial a_1}\right) \left(\frac{\partial w_x}{\partial w_z}\right) \underbrace{u(a_1, w_z)}_{=0} \\
 &= \left(\frac{\partial w_x}{\partial w_z}\right)^2 u^2(w_z) + \left(\frac{\partial w_x}{\partial a_1}\right)^2 u^2(a_1) + 2 \cdot \left(\frac{\partial w_x}{\partial a_0}\right) \left(\frac{\partial w_x}{\partial a_1}\right) u(a_0, a_1) + \left(\frac{\partial w_x}{\partial a_0}\right)^2 u^2(a_0) \\
 &\stackrel{\text{partial derivatives}}{=} \left(\frac{a_0}{a_1}\right)^2 u^2(w_z) + \left(-\frac{w_z \cdot a_0}{a_1^2}\right)^2 u^2(a_1) + 2 \cdot \left(\frac{w_z}{a_1}\right) \left(-\frac{w_z \cdot a_0}{a_1^2}\right) u(a_0, a_1) + \left(\frac{w_z}{a_1}\right)^2 u^2(a_0) \\
 &= \frac{w_x^2}{w_z^2} u^2(w_z) + \frac{w_z^2}{a_1^2} \left[\left(\frac{a_0}{a_1}\right)^2 u^2(a_1) - 2 \cdot \frac{a_0}{a_1} u(a_0, a_1) + u^2(a_0) \right].
 \end{aligned}$$

Modellgleichung:

$$w_x = \frac{a_0}{a_1} \cdot w_z$$

partielle Ableitungen

Aus den Unsicherheiten des OLS-Algorithmus folgt die relative MU:

$$u^2(a_0) = \frac{s_{xy}^2 \cdot \frac{1}{n} \sum_{i=1}^n x_i^2}{\sum_{i=1}^n (x_i - \bar{x})^2}, \quad u^2(a_1) = \frac{s_{xy}^2}{\sum_{i=1}^n (x_i - \bar{x})^2}, \quad u(a_0, a_1) = -\frac{s_{xy}^2 \cdot \bar{x}}{\sum_{i=1}^n (x_i - \bar{x})^2}$$



$$u_{\text{rel}}^2(w_x) = u_{\text{rel}}^2(w_z) + \frac{s_{xy}^2}{a_0^2} \cdot \left[\frac{1}{n} + \frac{\left(\frac{w_x}{w_z} + \bar{x}\right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right] \quad \text{mit} \quad \bar{x} = \frac{1}{n} \cdot \sum_{i=1}^n x_i \quad \text{und} \quad s_{xy}^2 = \frac{\sum_{i=1}^n [y_i - (a_0 + a_1 \cdot x_i)]^2}{n-2}$$

