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Introduction to Measurement Uncertainty

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CITAC
Cooperation on International Traceability in Analytical Chemistry

Eurachem
A FOCUS FOR ANALYTICAL CHEMISTRY IN EUROPE

Outline

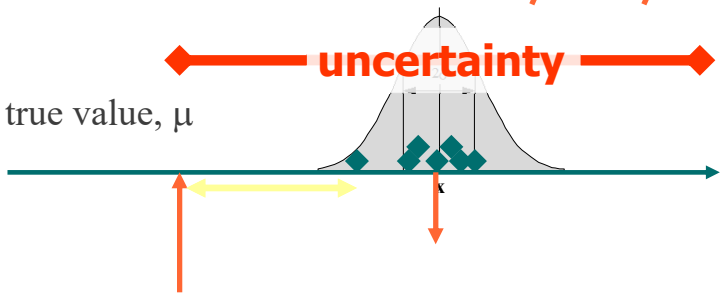
- What is measurement uncertainty?
- Quality from a customer´s perspective
- Monte Carlo simulation as a universal tool
- Special case of (large) relative uncertainty
- Remaining Problems: Inadequate results from Guidelines and Standards

Error of measurement vs. Uncertainty of measurement

(total) error of measurement =

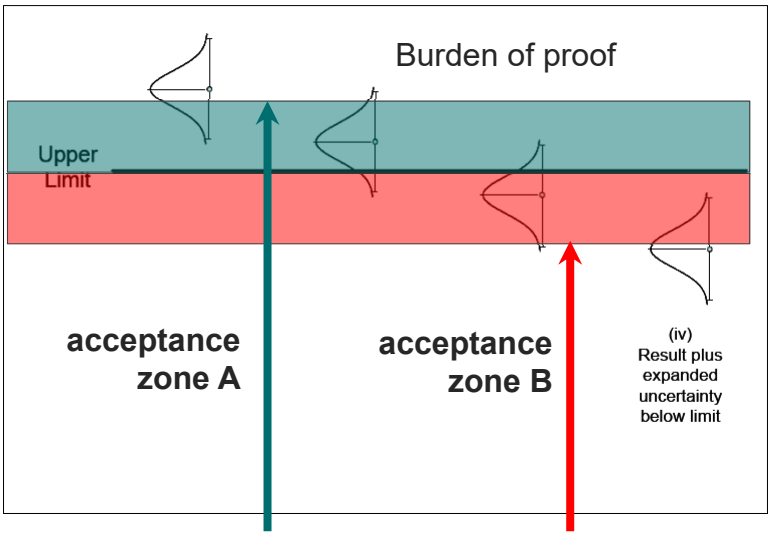
random error + systematic error

$$(x_i - \mu) = (x_i - \bar{x}) + (\bar{x} - \mu)$$



Decisions under uncertainty

Figure 1 Assessment of Compliance with an Upper Limit



Size of guard band g:
change k or u

$g = k * u = U \qquad k \propto (1-\alpha)_{CI}$

k...coverage factor

Greater k
leads to better coverage (subject to pdf)

but impairs decision process

Smaller u
leads to better decisions

but makes development of procedures and their operation more costly

http://www.eurachem.org/index.php/publications/guides/uncertcompliance

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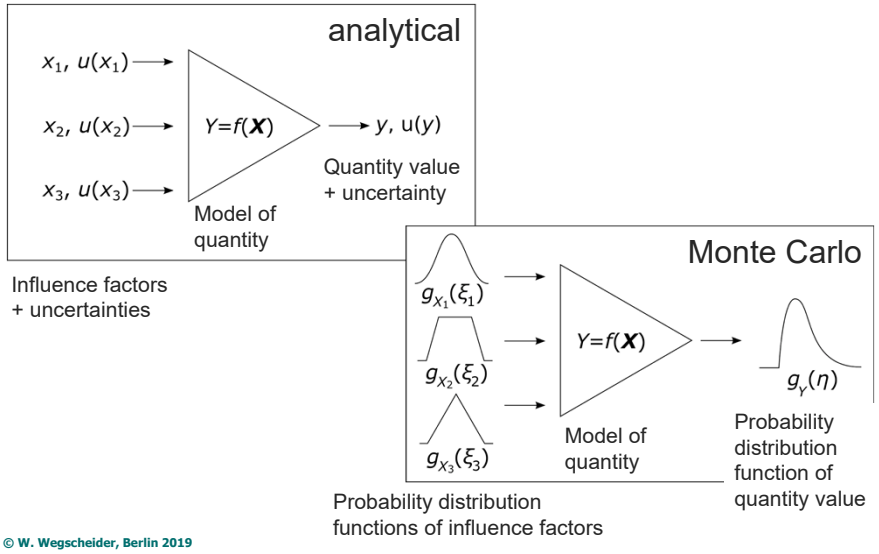
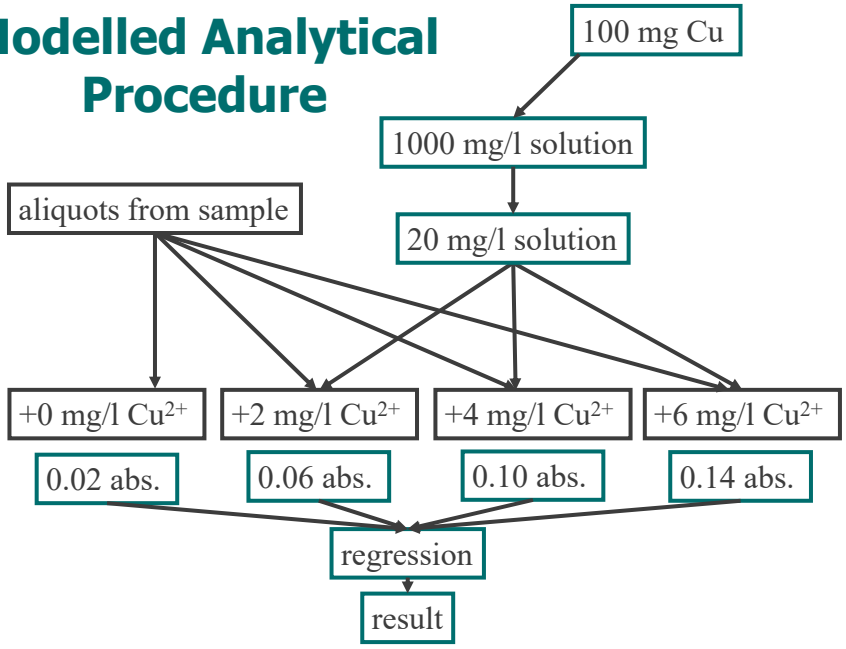
Analytical (and difference) vs. Monte Carlo



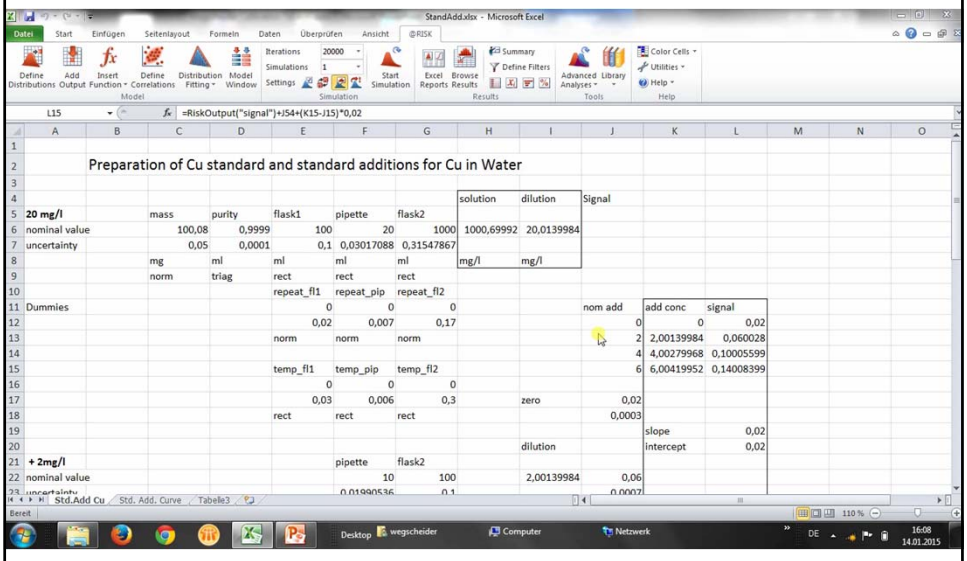
Uncertainty and Distribution from Standard Additions

- Textbook wisdom:
  - „extrapolation" to zero signal
  - asymmetric results for confidence limits
- Monte Carlo study with Excel add-in
- Determination of Cu by flame AA
  - Features: preparation of standards from solids, partial correlations, errors in x AND y

Modelled Analytical Procedure



17 s for a Monte Carlo simulation



StandAdd.xlsx - Microsoft Excel

=RiskOutput("signal")+J54+(K15-J15)*0,02

Preparation of Cu standard and standard additions for Cu in Water

							solution	dilution	Signal			
20 mg/l	mass	purity	flask1	pipette	flask2							
nominal value	100,08	0,9999	100	20	1000		1000,69992	20,0139984				
uncertainty	0,05	0,0001	0,1	0,03017088	0,31547867							
	mg	ml	ml	ml	ml		mg/l	mg/l				
	norm	triag	rect	rect	rect							
			repeat_fl1	repeat_pip	repeat_fl2							
Dummies			0	0	0				nom add	add conc	signal	
			0,02	0,007	0,17				0	0	0,02	
			norm	norm	norm				2	2,00139984	0,060028	
									4	4,00279968	0,10005599	
			temp_fl1	temp_pip	temp_fl2				6	6,00419952	0,14008399	
			0	0	0							
			0,03	0,006	0,3			zero	0,02			
			rect	rect	rect				0,0003			
										slope	0,02	
								dilution		intercept	0,02	
+ 2mg/l				pipette	flask2							
nominal value				10	100			2,00139984	0,06			
uncertainty				0,01990536	0,1				0,0007			

Std.Add Cu | Std. Add. Curve | Tabelle3

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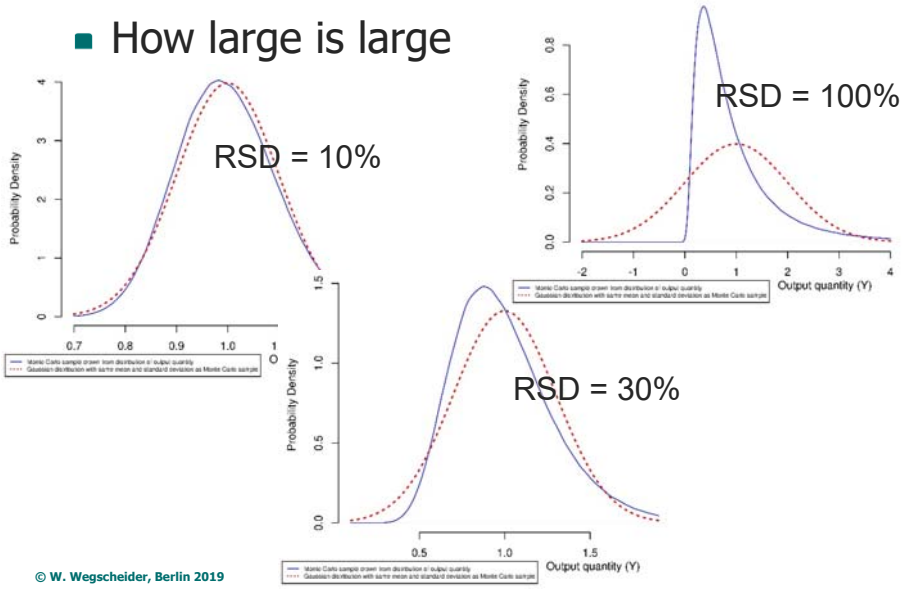
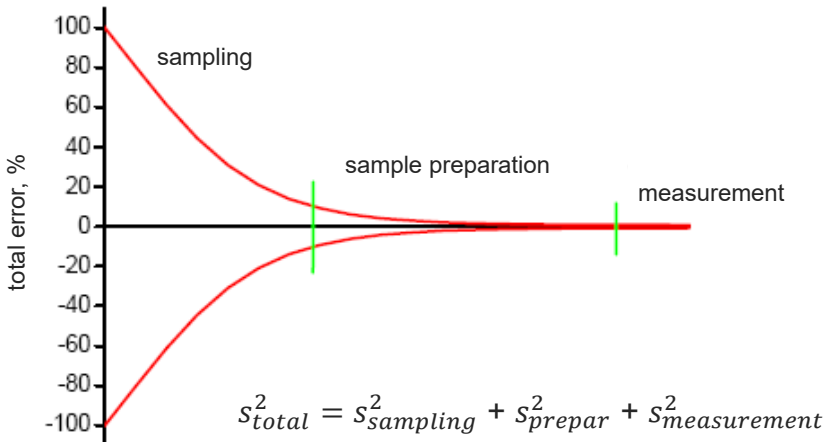
Large relative uncertainty

- How large is large



Typical contributions to uncertainty



$$s^2_{total} = s^2_{sampling} + s^2_{prepar} + s^2_{measurement}$$

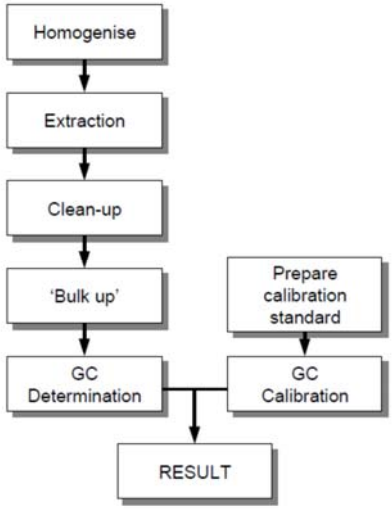
Consequences of typical contributions to uncertainty

$$s^2_{total} = s^2_{sampling} + s^2_{prepar} + s^2_{measurement}$$

- Sampling requires greatest attention
- Errors in sampling cannot be recovered in a later stage
- Only the largest contributions require optimization (Pythagoras !!!)

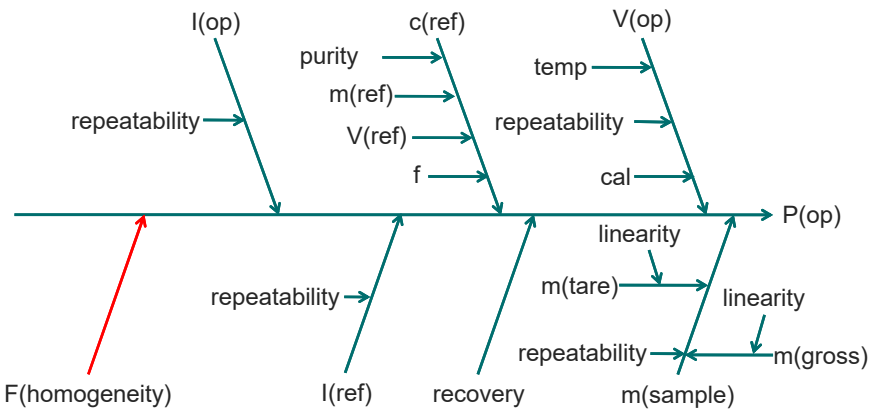
Determination of organo-phosphorus pesticides in bread

1. specification of measurand



Determination of organo-phosphorus pesticides in bread

2. identification of sources of uncertainty



Determination of organo-phosphorus pesticides in bread

3. Quantification of components

- Amended measurement equation:

$$P_{op} = \frac{I_{op} \cdot c_{ref} \cdot V_{op} \cdot 10^6}{I_{ref} \cdot m_{Probe} \cdot Rec} \cdot F_{\text{homogeneity}} \; (\mu g/g)$$

RSD = 27%

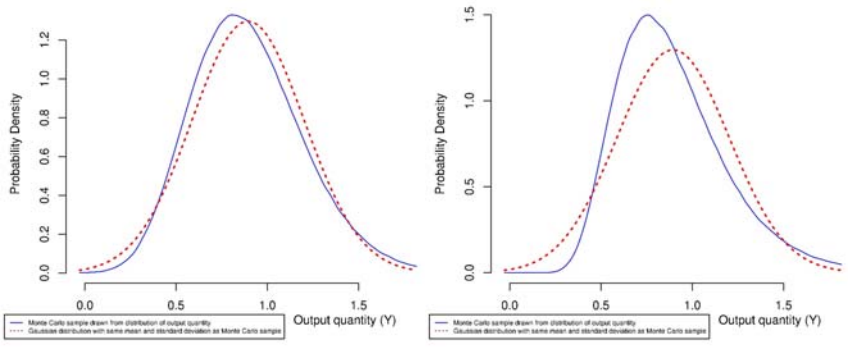
RSD = 20%

Determination of organo-phosphorus pesticides in bread

3. Combining the separate contributions

normal
95% (0.36;1.56)

log-normal
95% (0.44;1.63)



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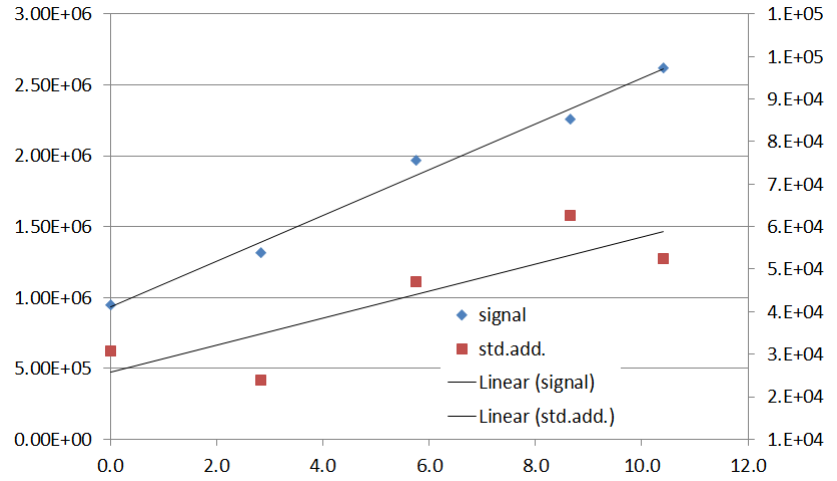
Standard on Standard Additions
DIN 32633 (2013)
5x5 additions

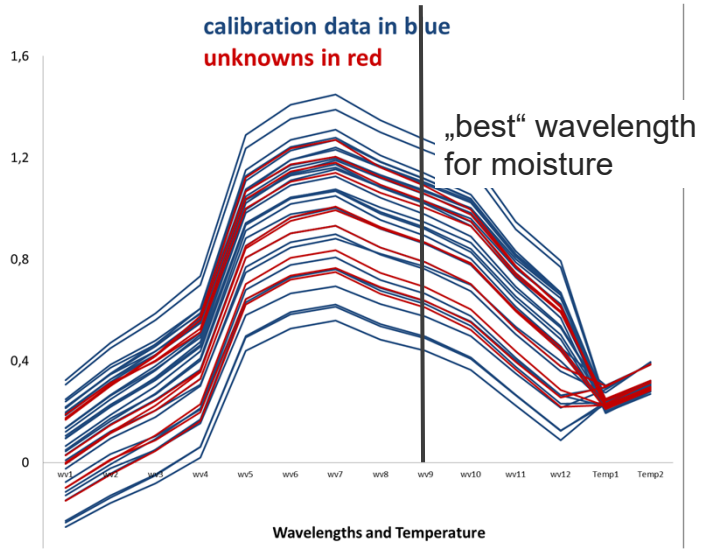
Ideal cases	s	result	DIN	M.C.
	Const. uniform	0.5 a.u.	0.060 a.u.	0.058 a.u.
	Const. normal	0.5 a.u.	0.027 a.u.	0.026 a.u.
Real cases	**from DIN/PTB**	µg/g		
Rh by ICPMS	increasing	231.3	12.9	5.6
Rh by ICPMS	intern. std.	233.7	3.3	2.2
		µg/ml		
Br ´ by IC	variable	24.44	0.54	0.25

ICP-MS Data from DIN

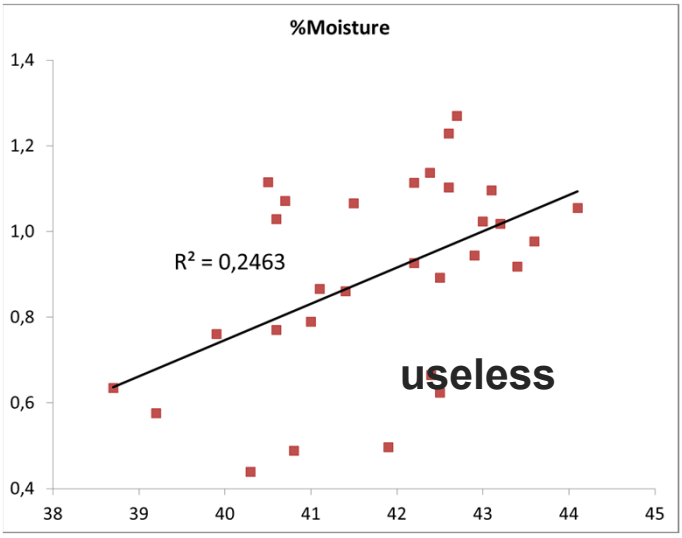


NIR spectra of brick cheese

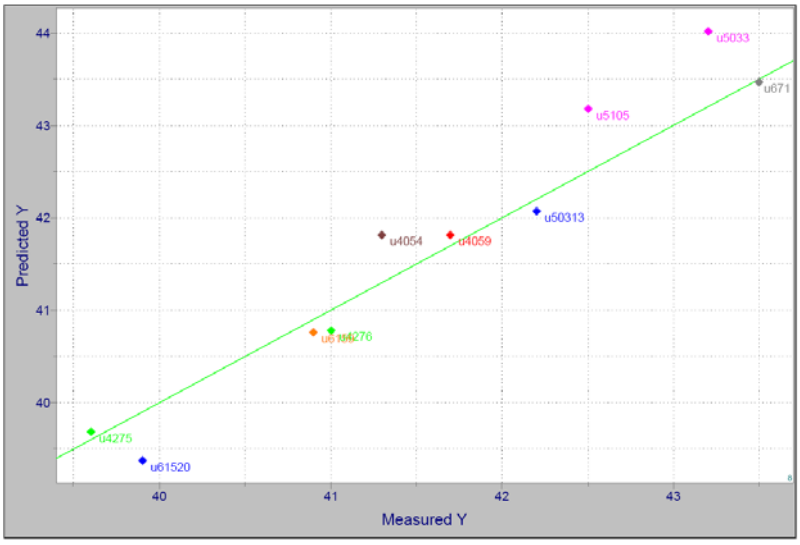
Infometrix Applications Overview 1996



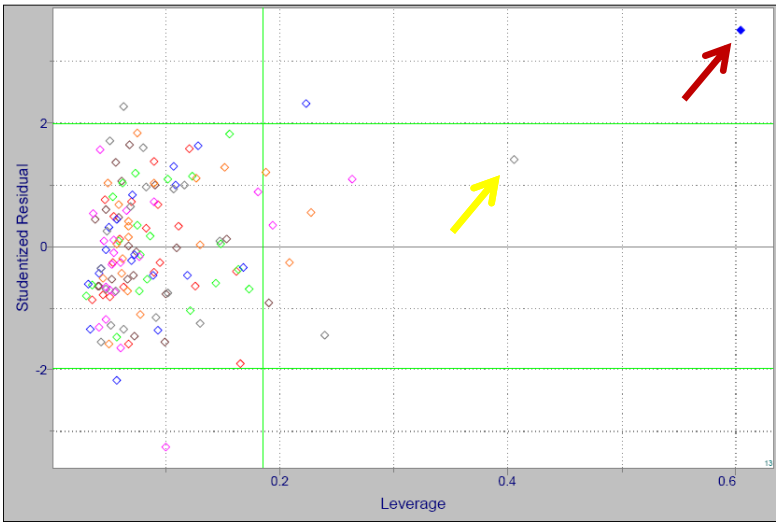
Calibration on wavelength 9



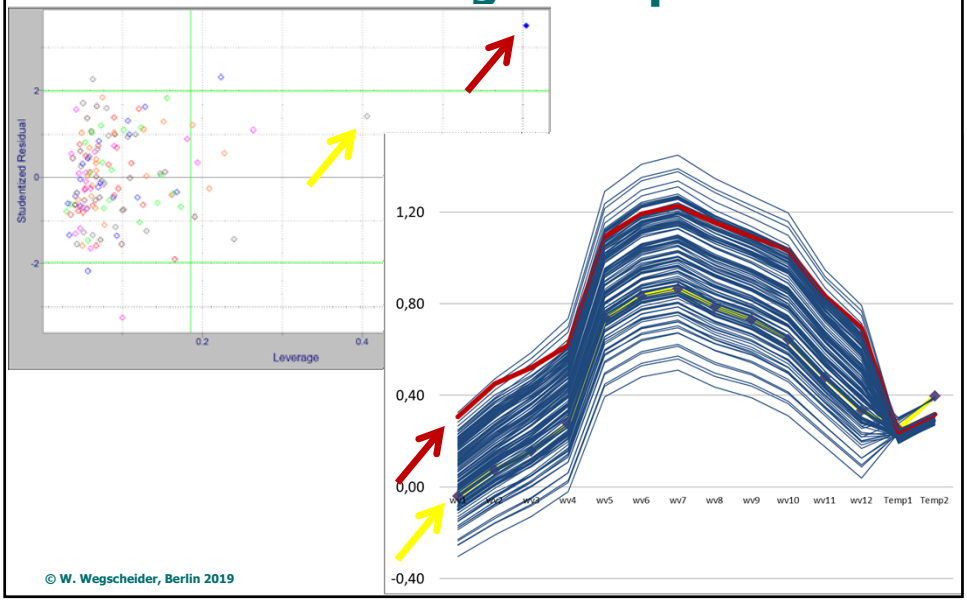
Multivariate prediction of moisture



h ..... leverage



h ..... leverage vs. spectra



IUPAC Approach to „uncertainty"

Pure Appl. Chem. 78, No. 3, pp. 633–661, 2006

$$\left[s(\mathrm{c})\right]^2 = hs_\mathrm{c}^2 + h(s_\mathrm{r}/S_n)^2 + (s_\mathrm{r}/S_n)^2$$

$\left[s(\mathrm{c})\right]^2$ variance of prediction

hs_c^2 leverage * var. of conc. of standards

$h(s_\mathrm{r}/S_n)^2$ leverage * var. of (signals/sensitivity)

$(s_\mathrm{r}/S_n)^2$ variance of (signals/sensitivity)

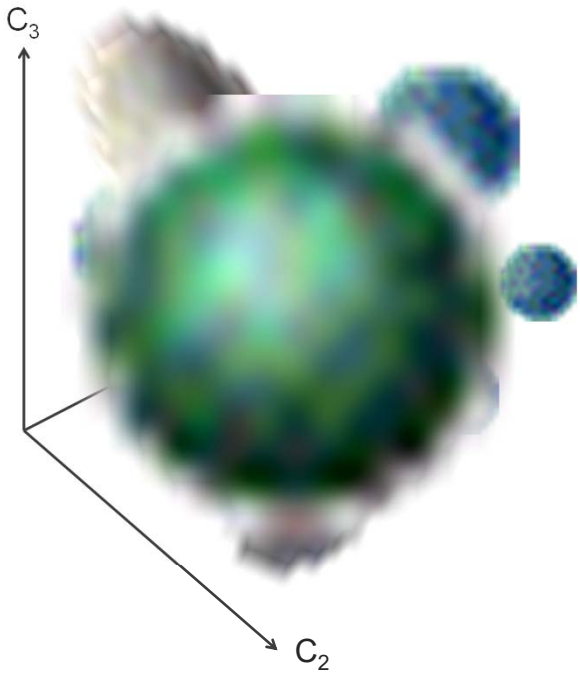
Effect as extra-RMSEP

in % moisture

Noise of 2% added to	Spectra of standards	Spectra of unknowns	Concen-tration of standards	Sum (IUPAC)	All three
Effect (in %moisture)	0.194				

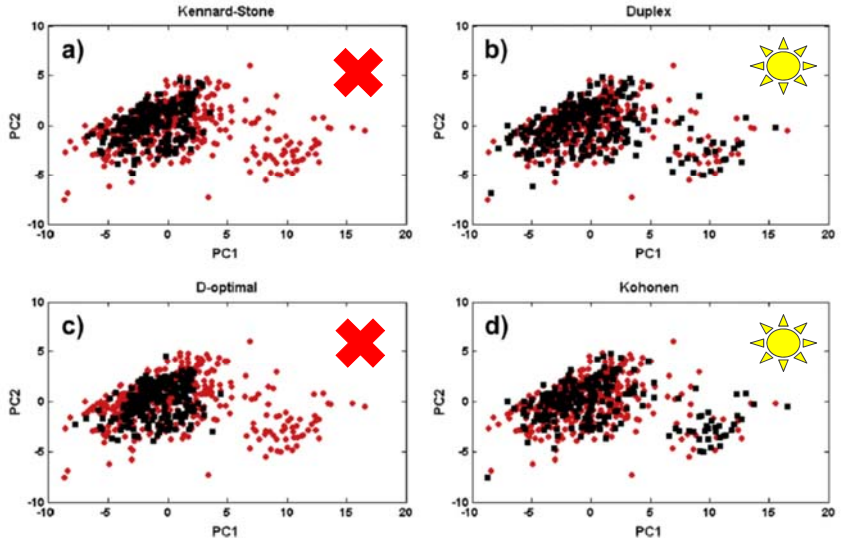
RMSEP = root mean squared error of prediction

- The IUPAC-proposed summation does not work
- Expected reason: no allowance for significant correlations
- Full Monte-Carlo procedure is required instead



Effect of four sampling procedures

Westad & Marini, 2015



Conclusions

- CITAC/Eurachem Guides have been very well received
- Very good tools are available for free
- Remaining problems should be tackled