

A systematic approach in the evaluation of uncertainty in analytical chemistry

Application to ICP-AES analysis

P.L. Carconi, R. Gatti, G. Zappa, C. Zoani



Dpt. Biotechnologies, Protection of Health and Ecosystems

*International workshop:
Combining and reporting analytical results.*

The role of (metrological) traceability and (measurement) uncertainty for comparing analytical results



APAT

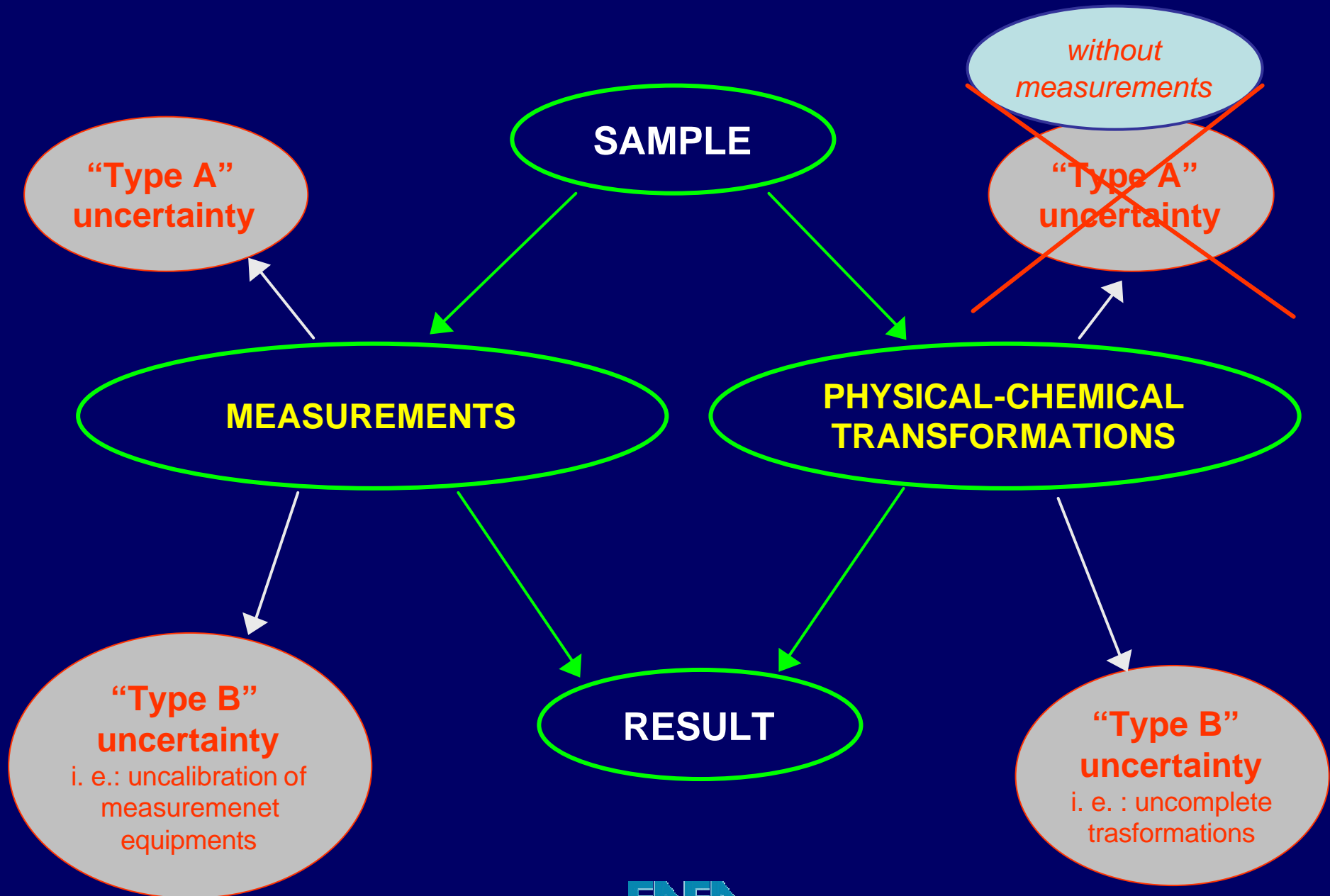
Agenzia per la protezione dell'ambiente
e per i servizi tecnici

Rome, 6-8 march 2006

Giovanna Zappa



MEASUREMENTS & PHYSICAL-CHEMICAL TRANSFORMATIONS



BREAK-DOWN

STEP 1

SAMPLING

laboratory sample

Sample storage

Sample preparation (ex.: homogenisation, drying, milling)

Sub-sampling

homogeneous sample

STEP 2

test-portion

Pre-treatment (ex.: weighing, dissolution, dilution)

Analyte measurement

Data processing

RESULT

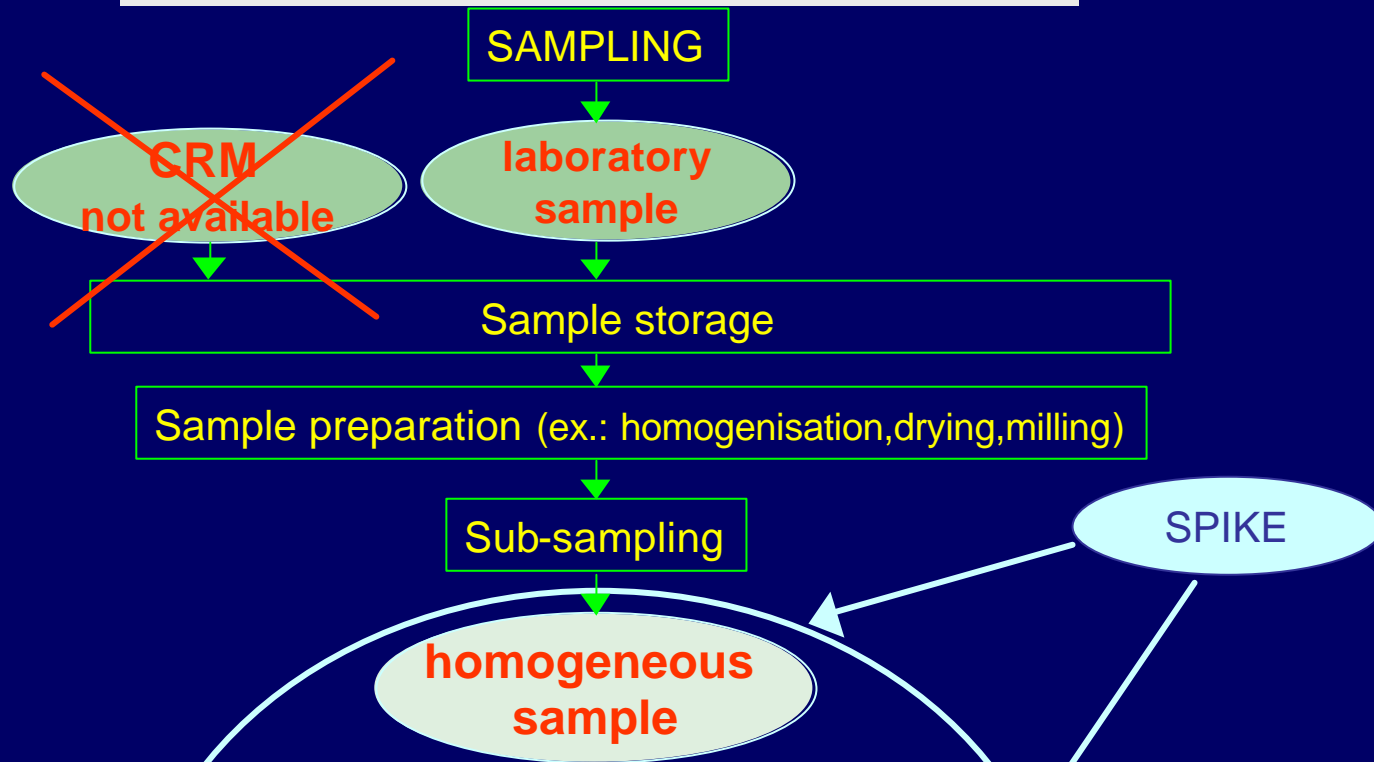
PHYSICAL-CHEMICAL TRANSFORMATIONS

Sample fractioning
Phase separation

MEASUREMENT PROCESS

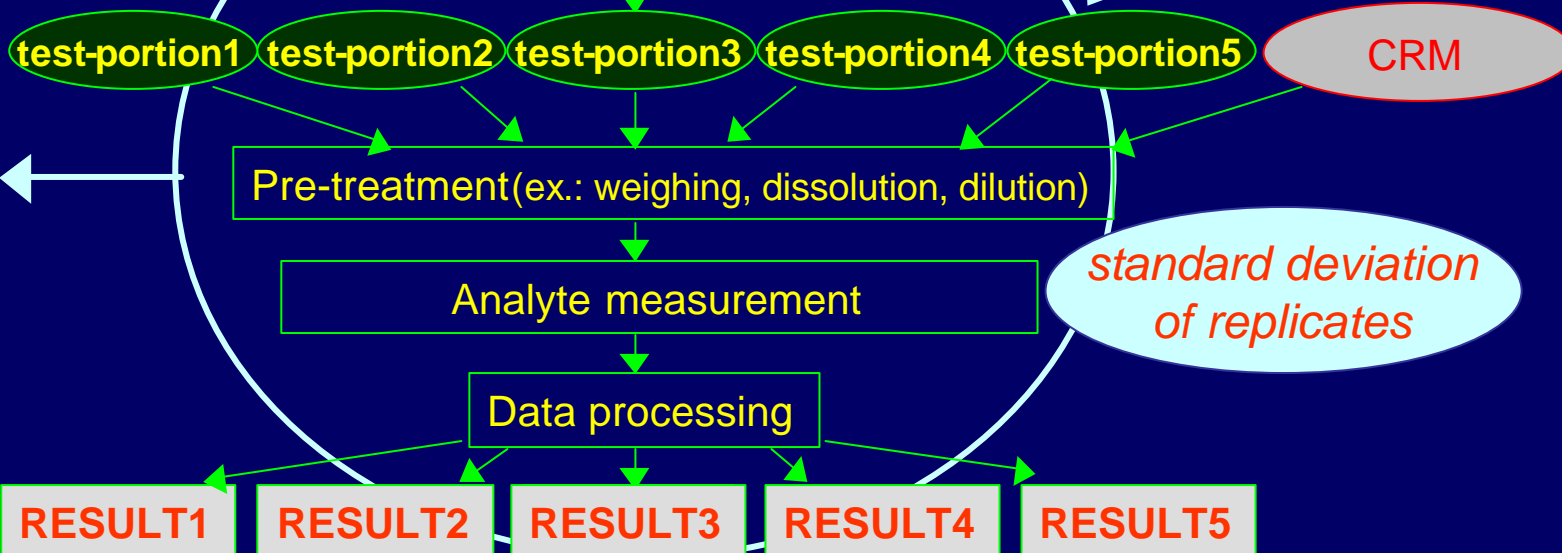
BREAK-DOWN ADVANTAGES

1

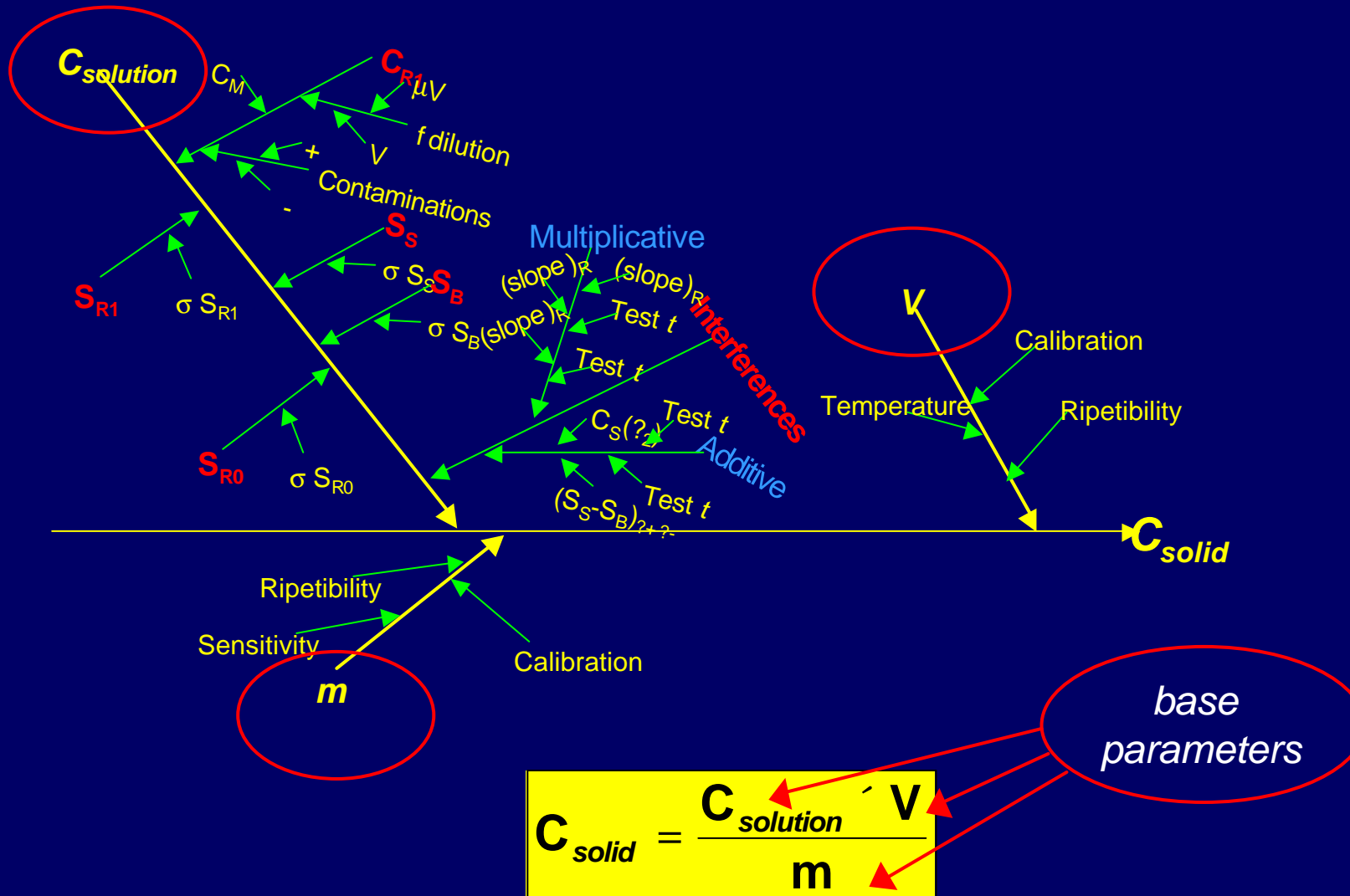


2

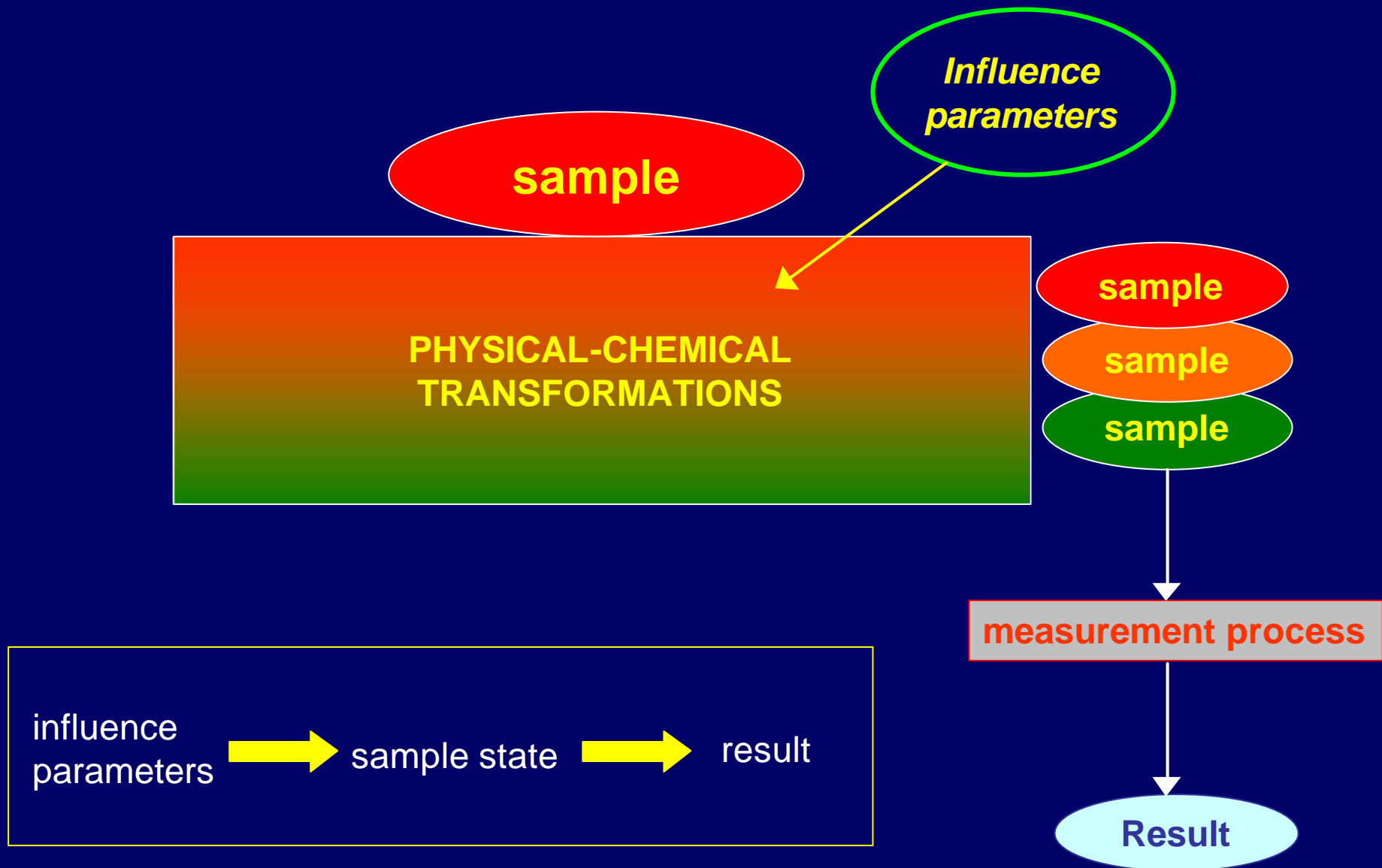
Recovery studies



UNCERTAINTY EVALUATION by *BOTTOM-UP* APPROACH



UNCERTAINTY RELATED to PHYSICAL-CHEMICAL TRANSFORMATION



AN ALTERNATIVE PATHWAY

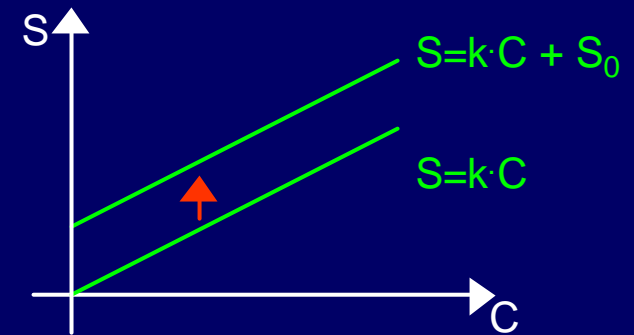
to evaluate the occurrence of systematic effects



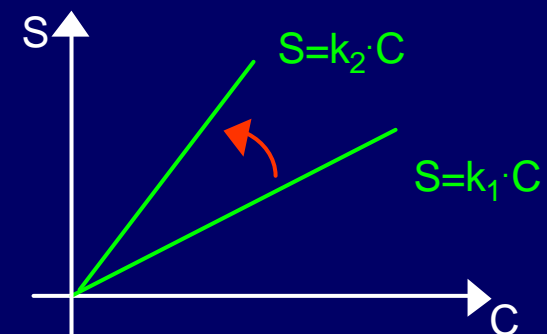
to use uncertainty related to this evaluation
for quantifying “type B” uncertainties

CLASSIFICATION of the SYSTEMATIC EFFECTS

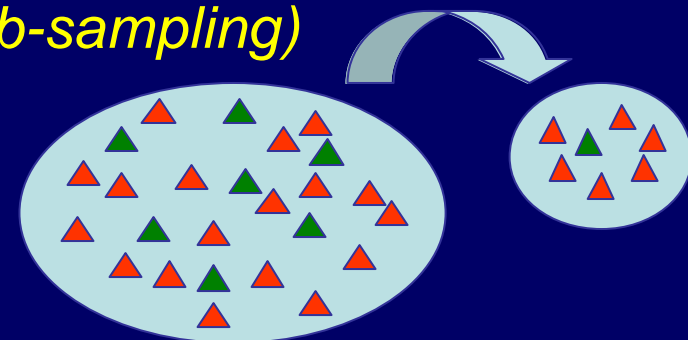
➤ Additive effects (*plus or minus*)



➤ Multiplicative effects



➤ Worsening of representativeness
(*i.e. inappropriate sampling or sub-sampling*)

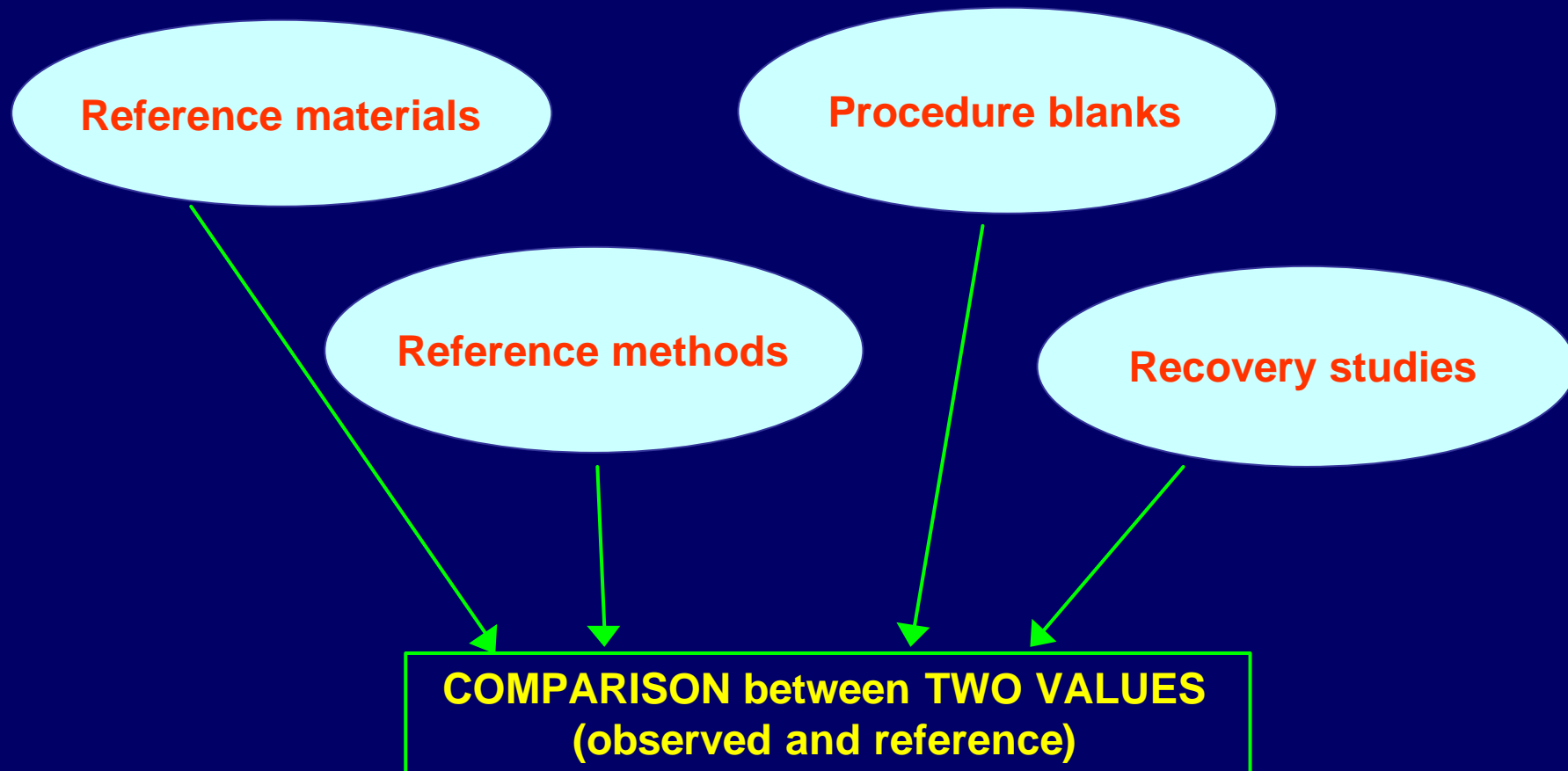


		Additive effects		Multiplicative effects	Worsening of representativeness
		+	-	X	
STEP 1 (from sampling to test portion)	Sampling	<i>I</i>			<i>P</i>
	Sample transport and storage	<i>I</i>	<i>I</i>		
	Sample preparation without fractioning or phase separation	<i>I</i>	<i>I</i>		
	Sample fractioning or phase separation	<i>I</i>	<i>I</i>	C, M, U	
	Sub-sampling (test portion picking out)	<i>I</i>			<i>P</i>
STEP 2 (from test portion to result)	Test portion size measurement (mass or volume)			<i>U</i>	
	Test portion pre-treatment and dilution	<i>I</i>	<i>I</i>	C, M, U	
	Analyte measurement	<i>I, C, M, U</i>	<i>I, C, M, U</i>	<i>C, M, U</i>	
	Data processing	<i>P</i>	<i>P</i>	<i>P</i>	

I = interactions between the sample and the environment or between the sample and the contact materials
C = experimental condition variations
M = matrix effects
U = un-calibration of measuring equipment
P = inappropriate procedure

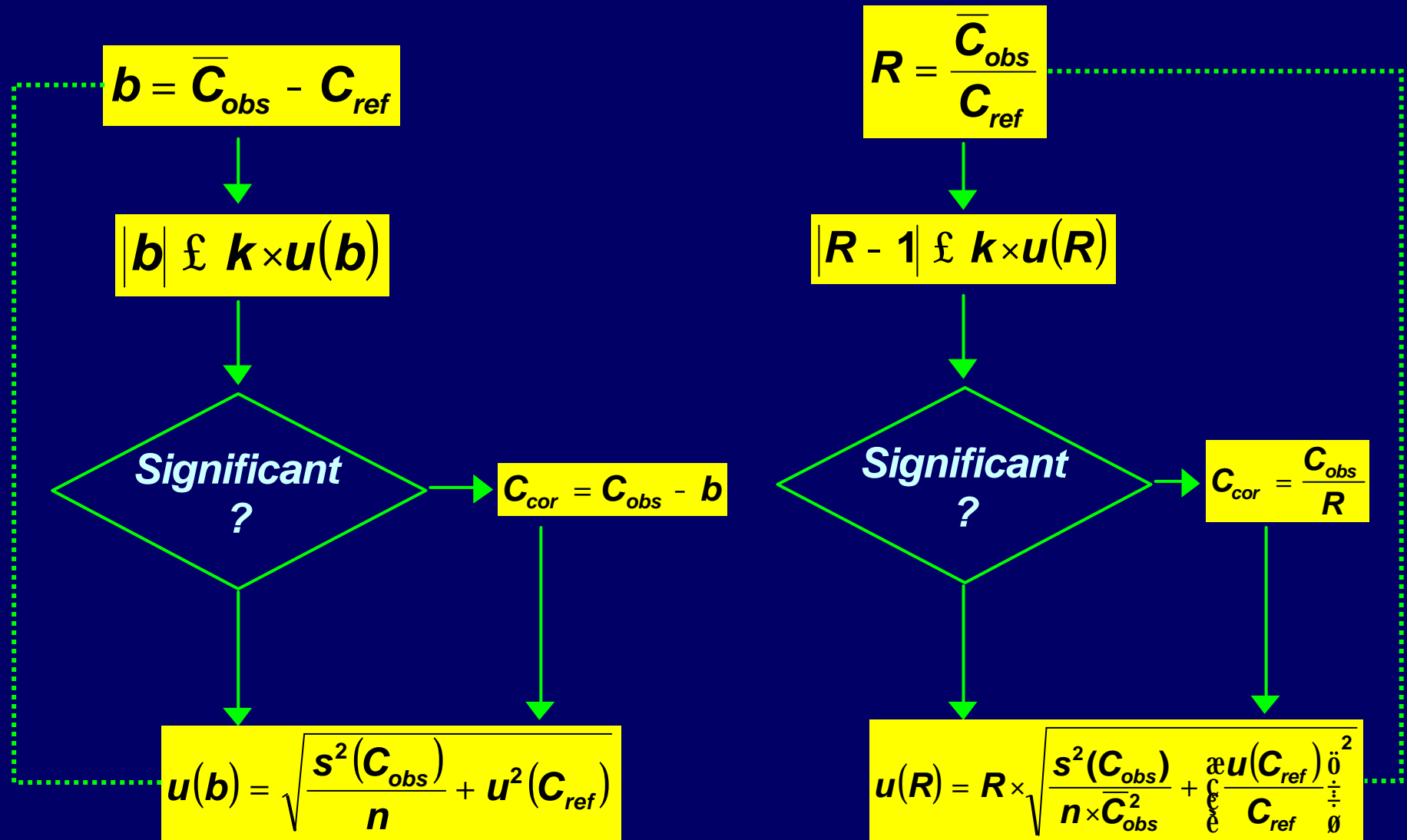


EVALUATION of BIAS EFFECT OCCURRENCE



Additive systematic effects

Multiplicative systematic effects



SYSTEMATIC EFFECTS EVALUATION by RECOVERY STUDIES

STEP 1

SAMPLING

laboratory sample

Sample storage

Sample preparation (ex.: homogenisation, drying, milling)

Sub-sampling

homogeneous sample

STEP 2

Reference (spike sample)

test-portion

Reference (CRM)

Pre-treatment (ex.: weighing, dissolution, dilution)

Reference (standard)

Analyte measurement

Data processing

RESULT

SYSTEMATIC EFFECTS EVALUATION by RECOVERY STUDIES

	Advantage	Application limits
matrix-CRM	<ul style="list-style-type: none">• allow to cover a large part of the measurement process	<ul style="list-style-type: none">• only for a few cases• very large uncertainty
pure-substance	<ul style="list-style-type: none">• available for almost all cases• narrow uncertainty	<ul style="list-style-type: none">• doesn't allow to cover the overall measurement process
spike-sample	<ul style="list-style-type: none">• available for many cases• narrow uncertainty	<ul style="list-style-type: none">• not sure about equilibrium between the analyte and the added substance
procedure-blank	<ul style="list-style-type: none">• permits to detect also very low contaminations	<ul style="list-style-type: none">• not sure about the same contamination degree

A PRACTICAL APPLICATION

Analysis of Ni in a vegetable sample by ICP-AES

REFERENCE

SAMPLE

BLANK

$$f_d = \frac{m_{dry}}{m_{wet}}$$

STEP 1

SAMPLING

Sample transport and storage

Sample preparation
(washing, homogeneization, milling, drying)

Sub-sampling

STEP 2

Weighing (m)

Reagent addition

Dissolution

Reagent addition

Dissolution

Mother reference
Solution (C_m)

DILUTION to C_{std}

Quantitative transfer
and filling up to fixed volume (V_1)

Measurement of the Ni concentration in solution (ICP-AES analysis)

Data processing

RESULT

$$C_{Ni} = \hat{e} \hat{e} \hat{e} \left(f_d \right) \times \frac{C_{std}}{I_{std}} \times I_{sample} \times \frac{V_1}{m} \hat{u} \hat{u} \hat{u}$$

“Type A” UNCERTAINTIES related to MEASUREMENTS of base parameters

$$C_{Ni} = \frac{\hat{e}}{\hat{e}} \times f_d \times \frac{C_{std}}{I_{std}} \times I_{sample} \times \frac{V_1}{m}$$

$$u_{typeA}(f_d) = f_d \times \sqrt{\frac{s_{m_d}}{m_d} + \frac{s_{m_w}}{m_w}}$$

$$u_{typeA} \left(\frac{V_1}{m} \right) = s_{rep}$$

$$u_{typeA} \left(\frac{C_{std}}{I_{std}} \right) = \frac{C_{std}}{I_{std}} \times \sqrt{\frac{u_{typeA}(C_m)}{C_m} + \frac{1}{n_1} \frac{s_{std}}{I_{std}} + \frac{s_{V_2}}{V_2} + \frac{s_{V_3}}{V_3}}$$

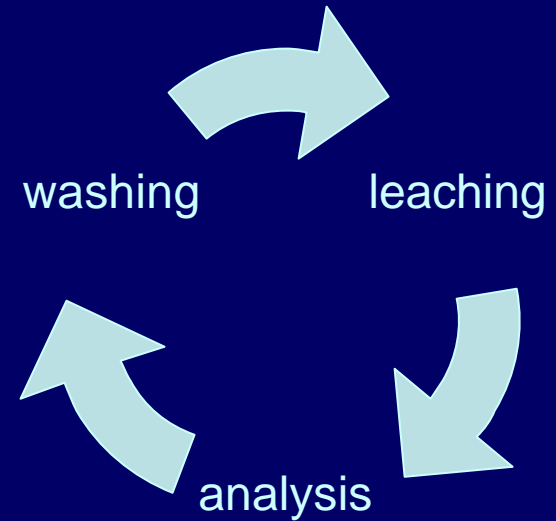
“Type B” UNCERTAINTY EVALUATION

EFFECTS CONSIDERED:

- uncertainty of the certified reference solution concentration
- un-calibration of measurement equipments
(as balance and calibrated glassware)
- sample contaminations during preparation and pre-treatment
- spectral interferences
- matrix interferences on sensitivity

SAMPLE CONTAMINATION EVALUATIONS

STEP 1
Storage, milling. Homogeneization,
Drying, sub-sampling



STOP → $C_{\text{blank}} < \text{D.L.}$
→ $C_{\text{blank}} = \text{Constant}$

STEP 2
Weighing, dissolution, dilution,
analysis



**Procedure
BLANKs**

SPECTRAL INTERFERENCES (additive)

$$(\bar{C}_{11} - \bar{C}_{12})$$

$$u(\bar{C}_{11} - \bar{C}_{12}) = \sqrt{\frac{s_{11}^2}{n} + \frac{s_{12}^2}{n}}$$

SPECTRAL INTERFERENCES (multiplicative)

$$u \frac{\bar{C}_{obs}}{\bar{C}_{ref}} = \sqrt{\frac{s_{obs}^2}{n \times \bar{C}_{obs}^2} + \frac{s_{ref}^2}{n \times \bar{C}_{ref}^2}}$$

CONCLUSIONS

- The “break down” of analytical procedure permits to group all the random effects for measuring “type A” uncertainty
- Bias evaluation is the most convenient way to estimate “type B” uncertainty caused by possible occurrence of systematic effects.

PROMPTS

**high pure
matrix reference materials
(HP-RMs)**

To evaluate bias due to sample contaminations

**INTERACTIVE
Instrumental-Operator
SOFTWARE**

To quantify measurement uncertainty