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**Workshop on Understanding and Evaluating Radioanalytical
Measurement Uncertainty**

5 - 16 November 2007

Estimation of Uncertainty arising from Sampling - Exercise

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I T A L Y*

Uncertainty
arising from sampling
Exercises

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Workshop on "Understanding and Evaluating Radioanalytical Measurement Uncertainty"

ICTP, Trieste (Italy), 5-16 November 2007

Contents

Two exercises:

1. **Empirical method (Duplicate)**

2. **Modelling method (Gy's Fundamental Error)**

Exercise 1
Empirical method-Duplicate

- A soil area was investigated in order to know the content of some trace element (As, Cr, Sc)

- 100 samples **(S1)** were collected by a stratified random strategy (100 sampling targets 10x10 m);

- Each sample was collected in duplicate **(S2)**;

- The duplicates were analysed in duplicate **(A1 and A2)**

Exercise 1

Measurand				Uncertainty estimation		
Analyte and technique	Unit	Matrix	Sampling target	Purpose	Design	Statistics
As, Cr, Sc INAA	mg kg^{-1}	Soil	Cell 10x10 m	▪Measurement uncertainty ▪Specific contribution from sampling and analysis	Empirical Duplicate Method	Robust ANOVA

Exercise 1

- Estimate for each and elements:
  - *Measurement uncertainty;*
  - *Sampling and analysis uncertainties;*
  - *The dominant component of uncertainty*

- Report the measurement result for a sampling target with the associated measurement uncertainty

Exercise 1

- ## Data:
  - ### DATA BASE_2.xls

- ## Calculation
  - ### ROBAN ver. 1.01

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Exercise 1

ROBUST ANOVA RESULTS:

Mean = 231,47298 mg/kg

Standard Deviation (Total) = 15,90858 mg/kg

	Geochemical	Sampling	Analysis	Measurement
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Standard Deviation	7,7554994	11,738699	7,4255023	13,890109
Percentage Variance	23,766035	54,447398	21,78657	76,233965
Relative Uncertainty	-	10,142609	6,4158697	12,001495
(% at 95% confidence)				

Exercise 2
Modelling approach
Gy's Fundamental Error

- Particulate material has to be analysed for Pb content (contamination)

- The primary sample is taken from a very large lot

- The study design objectives require:
  - an analysis using a maximum **test portion** of **5 g**;
  - Maximum sampling fundamental error of **8 %** ($S^2_{FE} = 6,4 \times 10^{-3}$) of the mean Pb mass fraction

- Different sub-sampling and comminution steps are performed

- Analytical uncertainty equals to **5%** of the mean Pb mass fraction

Exercise 2

Measurand				Uncertainty estimation		
Analyte and technique	Unit	Matrix	Sampling target	Purpose	Design	Statistics
Pb ICP-OES	mg kg^{-1}	Soil	Primary sample	Sampling Fundamental Error	Modelling Gy's theory	Propagation of error

Exercise 2

- Estimate :

  - *Contribution of each sampling step to the whole Sampling Fundamental Error;*

  - *Sampling Fundamental Error ;*

  - *The dominant contribution*

- Is the sampling procedure fit-for-purpose ?

Exercise 2

- Data:
  - **Template Gy**

Exercise 2 - comment

- The dominant contribution to the Fundamental sampling error is attributed to:

- **Template Gy_solved.xls**