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Data combination strategies:

Approaches and examples from BAM expertise in RM certification

Topics:

- Introduction
- Consolidation in 3 steps
- Sources of, and tools for, bias investigation
- Examples: Bi determination (uses GLS)
  Water in glass (model as a source of bias)
  Purity analysis (uses MANOVA and weighted mean)
- Conclusions

Introduction

Combining (consolidating) results from different measurements = investigation of result (in)compatibility within stated, assigned, or "classically" calculated uncertainties.

Selection of an appropriate consolidation strategy (including a corresponding uncertainty estimation) depends on the outcome of the above investigation.

Any strategy is inappropriate if it fails to provide sufficient proof of compatibility of the final result with the data combined. The E_n criterion (or derivatives) is convenient and widely applicable to this specific task.

Data consolidation in three steps

Step 1: Data inspection and pre-treatment (if necessary)

Step 2: Data exploration (bias detection)

Step 3: Appropriate combination of data

no bias detected: ”pooling”, i.e. appropriate average and uncertainty estimate for single values

bias detected: ”no pooling”, i.e. groupwise, hierarchical consolidation starting from the highest subgroup level for which no bias was detected between group members
appropriate average and uncertainty estimate which takes up the uncertainties calculated at lower consolidation levels, e.g.:

$$x_1, \ldots, x_n$$

$$u(x_1), \ldots, u(x_n) \quad \Rightarrow \quad u^2(x_a) = s^2/n + \sum u^2(x_i)/n^2$$

Sources of, and tools for, bias investigation

Sources:

sample inhomogeneity

sampling process variability

sample instability

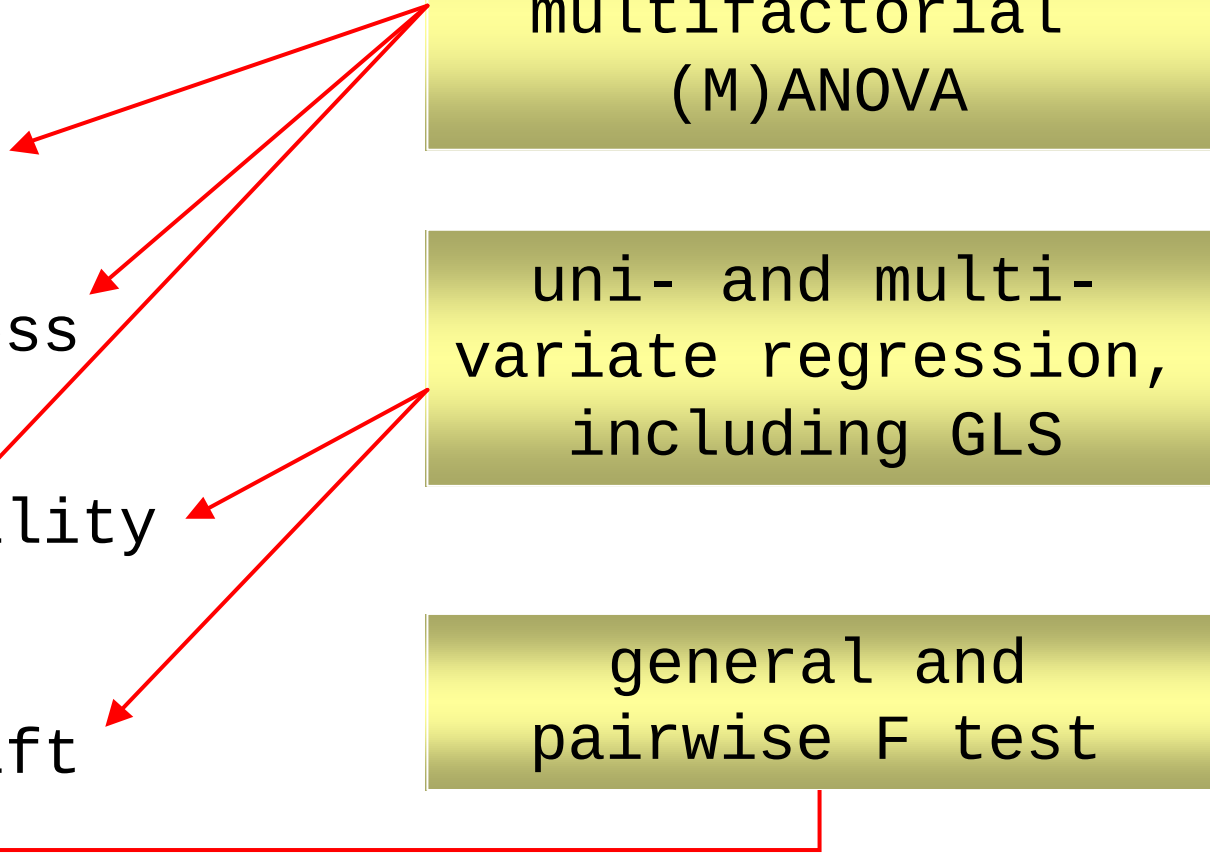
method bias

instrument drift

one- or multifactorial (M)ANOVA

uni- and multi-variate regression, including GLS

general and pairwise F test



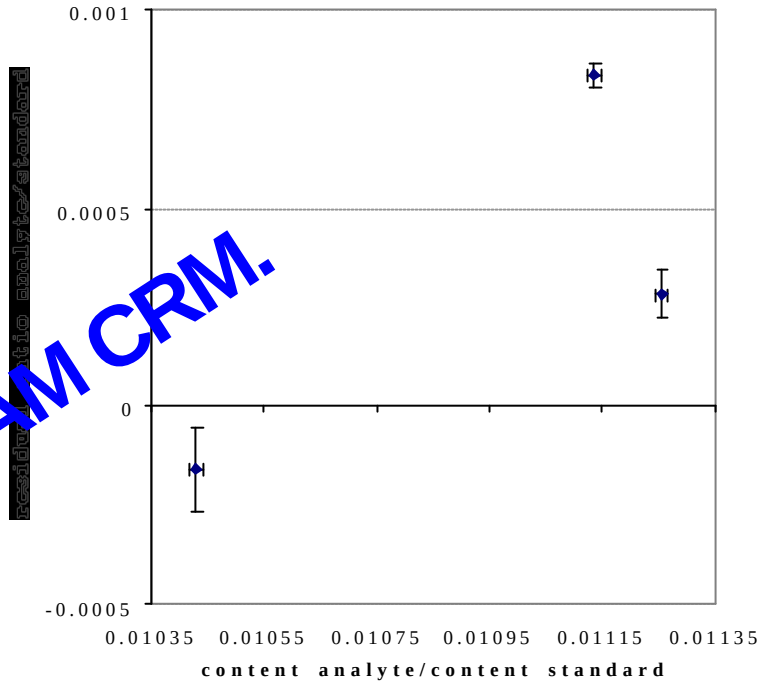
Bi determination: GLS

Certification of a calibration solution for Bi content

method:
high-performance ICP-OES using internal standard

SOP:
8 calibrant solutions from 4 parent solutions
calibration of the instrument (ratio/ratio)
measurement of 6 samples of the unknown
averaging

prelim value 10.094 ± 0.0065 mg/g



This is not a BAM CRM.

residual SSD = 1710.6, GoF = 24.92

correct value 10.094 ± 0.023 mg/g

certified value 10.00 ± 0.01 mg/g

Water in glass: Model as a source of bias (1)

hydrogen content determination by NRA

$$^{1}H(^{15}N, \alpha\gamma)^{12}C$$

$$x_{Probe}^{NRA} = \frac{S_{Probe}}{S_{Standard}} \cdot \frac{Y_{Probe}}{Y_{Standard}} \cdot x_{Standard}$$

S - stopping power
Y - counts for sample and standard
x - H content for sample and standard

OH bond (water) concentration determined by FT-IR

$$c_{H_2O}^{IR} = \frac{\alpha_{3550} - \alpha_{4000}}{\varepsilon_{3550}} + \frac{4}{3} \cdot \frac{\alpha_{2800} - \alpha_{4000}}{\varepsilon_{2800}}$$

α - absorption coefficient at wavenumber...
ε - (model) extinction coefficients

both legs: 3 disks, 24 chips each, selected measurements taken, 2way ANOVA

$$u^2(x_{NRA}) = \frac{s}{\sqrt{n}} + u^2_{inhom\ disk-to-disk} + u^2_{inhom\ on-disk} + u^2_{method}$$

Water in glass: Model as a source of bias (2)

(values in mol/L)

	H2O from H		H2O		E_n
305_96	0.03169	0.00091	0.03446	0.00025	2.91512
274_00	0.03303	0.00089	0.03597	0.00017	3.23641
215_03	0.03319	0.00095	0.03440	0.00014	1.26186
total	0.03264	0.00130	0.03494	0.00102	1.39851

model error:

i) bias in extinction coefficients

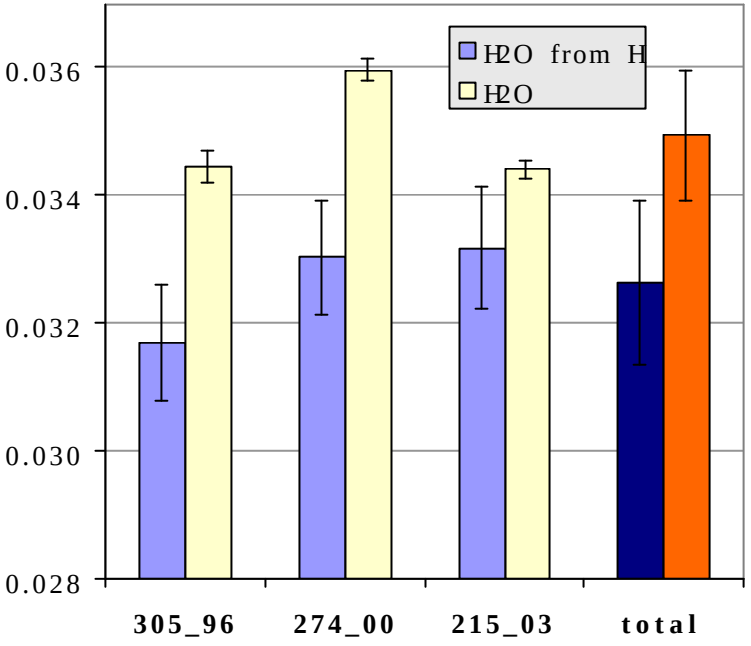
ii) hydrogen other than in an OH bond

$$c^{IR}_{H_2O} = (f + \delta) \cdot c^{NRA}_{H}$$

$$c^{IR}_{H_2O} = f \cdot c^{NRA}_{H} + \delta \cdot c_{XH}$$

	H2O from H		H2O		E_n
	0.032638	0.001296	0.034943	0.001019	1.39851
u_extension		0			

	H2O from H		H2O		E_n
	0.032638	0.001726	0.034943	0.001529	1.00000
u_extension		0.00114			



weighted mean	**0.03393**	mol/l
u(mean)	**0.00145**	mol/l

Purity analysis: MANOVA and weighted mean (1)

target: certification of o-xylene for purity

methods

DSC: Calibrated method using intentionally contaminated o-xylene calibration solutions, assessment from calibration experiment including weighing uncertainties.

GC trace analysis: Calibrated method using gravimetrically prepared calibration solutions, assessment from the calibration experiment including weighing uncertainties.

mean + unc

Column 1 → **Column 2** → **MANOVA** → **mean + unc(..., bias)**

mean + unc

100% GC/FID: A-type base line noise and peak area SD evaluation for each analyte, propagation via the normalisation function (7 and 9 replicates), inclusion of unidentified tiny peak in u_total.

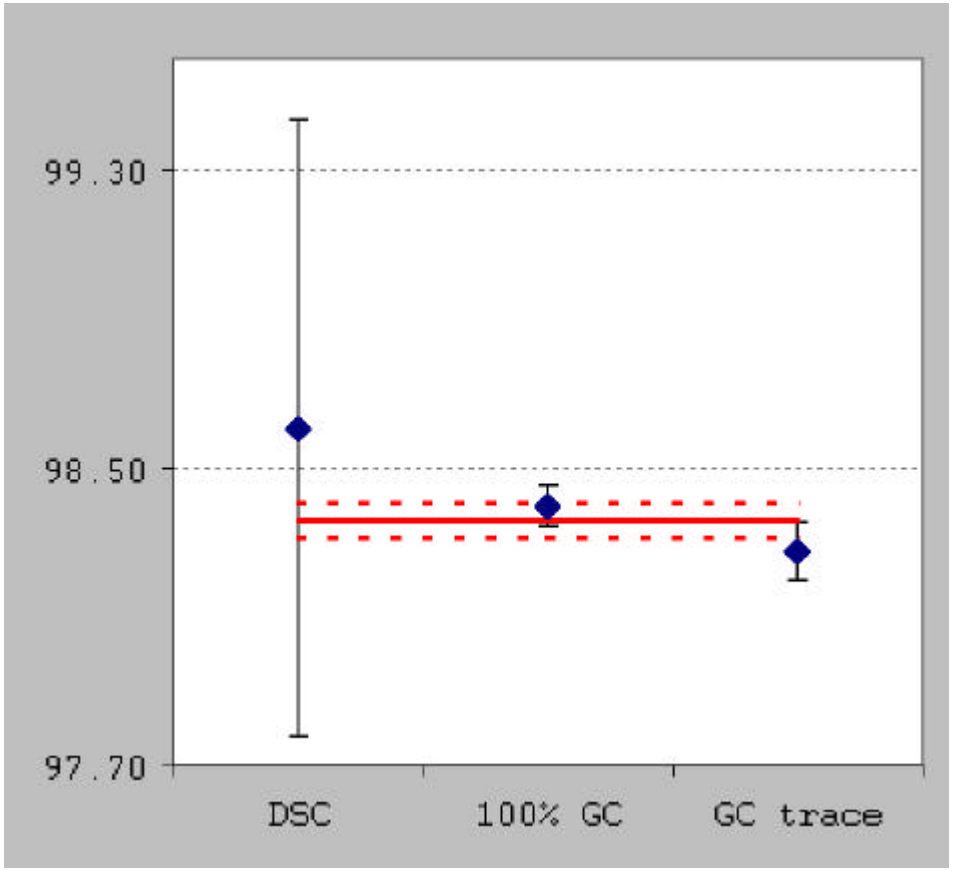
100% GC/FID calibrated using intentionally contaminated o-xylene (for blunder check)

Column 1 → **Column 2** → **MANOVA**

	benzene	toluene	ethylbenzen	m, p-xylene	total
100% GC:	0.236	0.458	0.709	0.185	1.588
	0.009	0.020	0.029	0.007	0.037
GC trace:	0.240	0.492	0.776	0.216	1.724
	0.017	0.053	0.043	0.032	0.078
E_n	0.18643975	0.59716331	1.28616336	0.94719635	1.5776716

Purity analysis: MANOVA and weighted mean (2)

	value	uncertainty
DSC	98.61	0.83
100% GC	98.40	0.06
GC trace	98.28	0.08
weighted mean:		**98.36**
uncertainty:		**0.05**
GoF:		1.00
effective DoF:		7
CI:		0.11



=> elegant approach to incorporate independent methods having larger uncertainties

Conclusions

- Any data consolidation strategy starts from thorough data exploration aiming at the detection of possible bias.
- Plenty of tools exist. Which tools are appropriate depends on the suspected sources of bias. Multi-analyte analyses require multivariate data exploration tools.
- Complete uncertainty budgets should be the basis for exploration. Bare repeatabilities are normally insufficient.
- The outcome of data exploration suggests the appropriate way of combining results.
- Data consolidation was successful if individual data are compatible with the final result within the stated uncertainties (assessed by E_n criterion or Birge ratio).

Thank you for your attention!