Bayesian analysis of homogeneity studies in the production of reference materials

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Rationale

- Well known that the repeatability standard deviation (σ) sets a lower limit to the determination of the between-bottle standard deviation (τ)
- Increase of the number of replicates not always possible
- Need for a statistically sound approach for monitoring the performance of a decanting method for synthetic natural gas mixtures

Repeatability standard deviations of the natural gas analyser

Table: Amount-of-substance fractions (x) expressed in % and repeatability relative standard deviations (s) for natural gas

	x	s
ethane	3.4978	0.012 %
propane	4.7007	0.010 %
iso-butane	0.1234	0.011 %
n-butane	0.1225	0.012 %
iso-pentane	0.0306	0.031 %
n-pentane	0.0312	0.021 %
n-hexane	0.0760	0.014 %
carbon dioxide	5.0327	0.023 %
nitrogen	0.4251	0.165 %
methane	85.9601	0.011 %

Computation of the between-bottle standard deviation

- Compute the between-group variance

$$\tau^2 = \frac{MS_{\text{between}} - MS_{\text{within}}}{n}$$

- Problems arise when $MS_{\text{between}} < MS_{\text{within}}$

Table: ANOVA results for nitrogen

Source of Variation	*SS*	ν	*MS*	*F*
Between Groups	2.92×10^{-10}	9	3.25×10^{-11}	0.663
Within Groups	1.96×10^{-9}	40	4.90×10^{-11}	
Total	2.25×10^{-9}	49		

Alternatives if $MS_{\text{between}} < MS_{\text{within}}$

- set $\tau = 0$ (e.g., ISO 13528:2015, ISO Guide 35:2017)
- set $\tau = \sqrt{\frac{MS_{\text{within}}}{n}}$ (Ellison, 2015)
- set $\tau = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt[4]{\frac{2}{\alpha(n-1)}}$
  (Van der Veen et al., 2001; ISO Guide 35:2017)

Bayesian modelling

- “Solution” published in 2001 has never been viewed as entirely satisfactory
- None of the three options permits a judgment on the performance of the decanting method
- Bayesian inference will provide a posterior probability distribution for τ
- Mean of the probability distribution of τ can be taken as the estimate for the between-bottle standard deviation

Bayesian model (1)

- Same underlying assumptions for the data
  - normally distributed data
  - homogeneity of the within-group standard deviations
  - no substantial prior information
- Same statistical model as used in 2001 with classical analysis of variance

$$y_{ij} = \mu + B_i + \varepsilon_{ij}$$

where y_{ij} denotes the jth replicate on the ith mixture, μ the amount-of-substance fraction, B_i the bias of ith mixture, and ε_{ij} the measurement error

Bayesian model (2)

- Model parameters:
  - Batch value for the amount-of-substance fraction μ
  - Within-group variance $\sigma^2 = \mathrm{var}(\varepsilon_{ij})$
  - Between-group variance $\tau^2 = \mathrm{var}(B_i)$
- For each of the parameters, a prior probability distribution is to be assigned

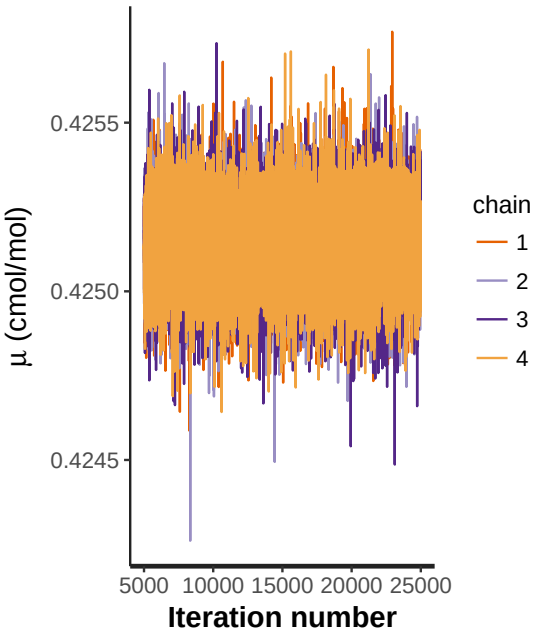
Prior distributions

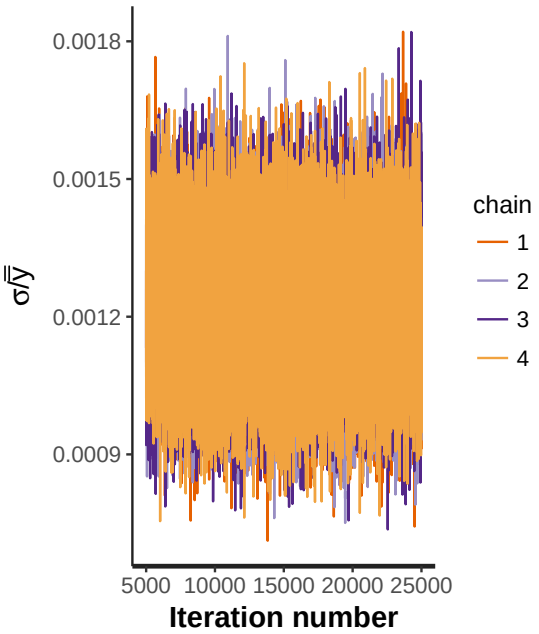
- Non-informative priors do not really reflect the information available
- Weakly informative priors
  - allow a (weak) influence of our prior information (nominal amount-of-substance fraction, repeatability standard deviation, between-bottle standard deviation)
  - improve performance of the Markov Chain Monte Carlo method (MCMC)
  - do not require proving that the posterior probability distribution is “proper”
  - should be assessed for actually behaving as “weakly informative”

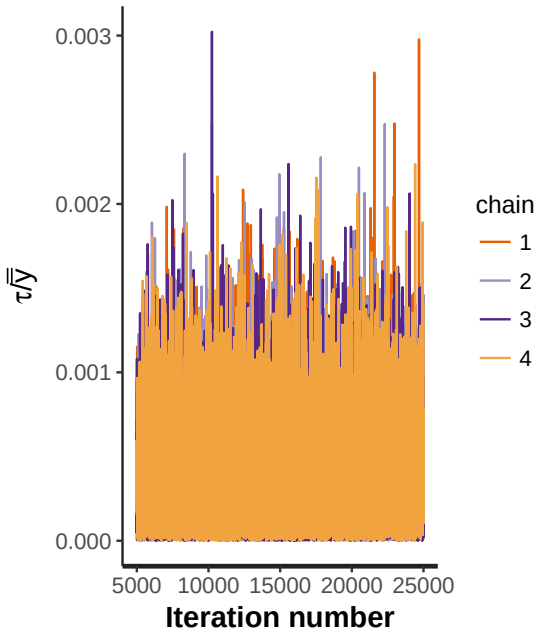
Bayesian model (3)

- $\mu \sim \mathrm{N}(\mu_0, \sigma_0^2)$; $\sigma_0 = 0.05\mu_0$
- $\sigma \sim \mathrm{Cauchy}(0, A_\sigma)$; $A_\sigma = 2\max_i(s_i)$
- $\tau \sim \mathrm{Cauchy}(0, A_\tau)$; $A_\tau = 5s_1$
- Parameters for the folded Cauchy-distribution (t-distribution with $\nu = 1$) set sufficiently wide to ensure "weakly informative" behaviour

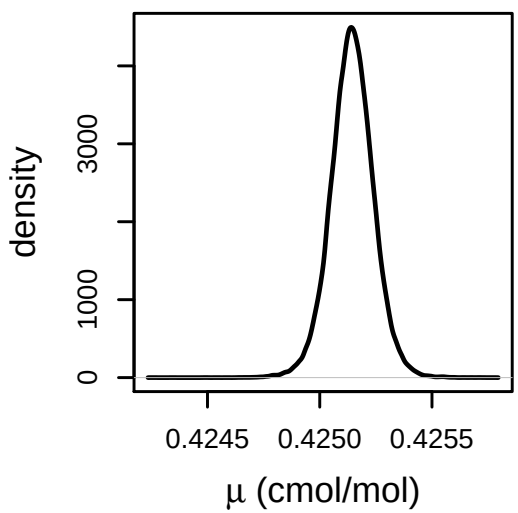
Trace plots nitrogen

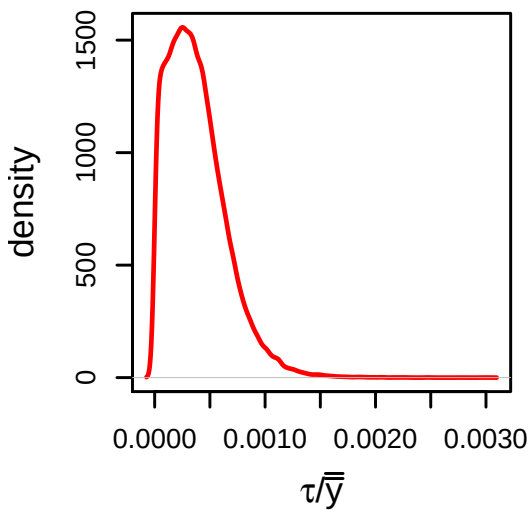


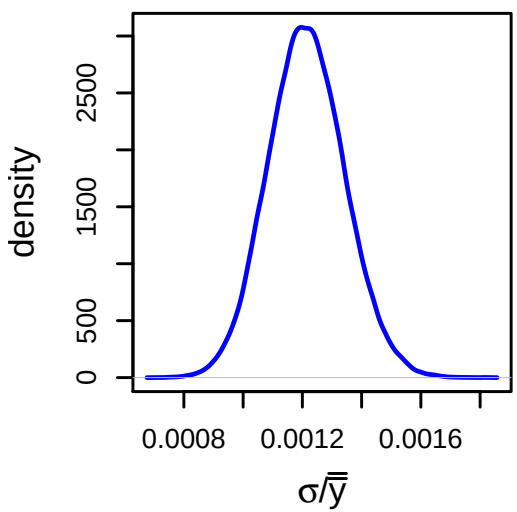




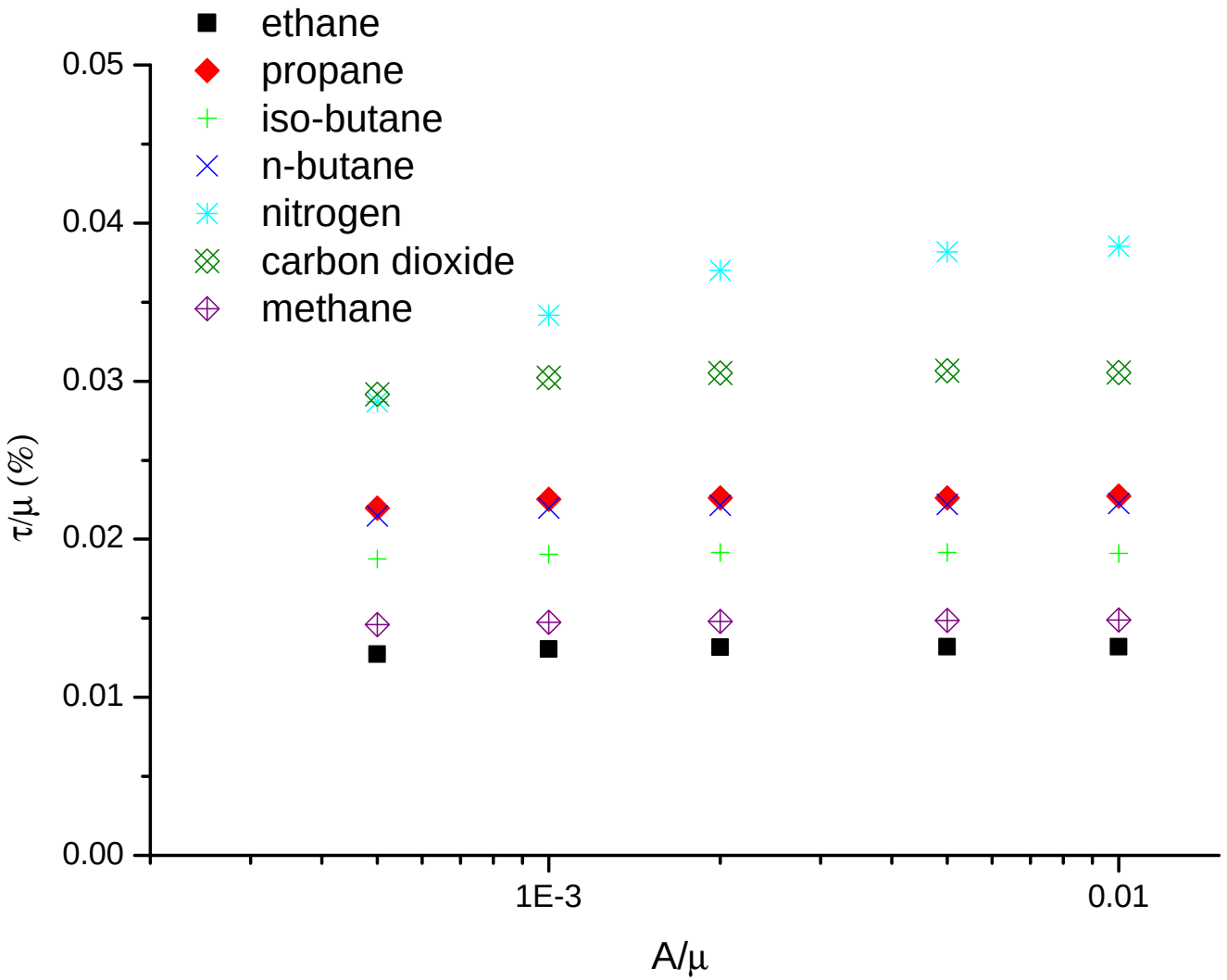
Posteriors for μ, σ and τ for nitrogen







Sensitivity analysis



Nitrogen: results and the alternatives

Table: Results of the MCMC calculation for nitrogen.

	mean	sd	$q_{0.025}$	$q_{0.975}$
μ	0.425 144 3	0.000 168 0	0.424 812 2	0.425 475 7
τ	0.000 172 0	0.000 143 9	0.000 006 1	0.000 532 0
σ	0.000 480 8	0.000 055 7	0.000 375 2	0.000 593 5

- Bayesian model: $\hat{\tau} = 1.72\,\mu\text{mol}\,\text{mol}^{-1}$, which lies in between
- ISO Guide 35: $u^*_{\text{bb}} = 1.48\,\mu\text{mol}\,\text{mol}^{-1}$ and
- Elisson: $\sqrt{MS_{\text{within}}/n} = 3.13\,\mu\text{mol}\,\text{mol}^{-1}$.
- Both u^*_{bb} and $\sqrt{MS_{\text{within}}/n}$ within the 95 % coverage interval of τ.

Conclusions

- Bayesian analysis is to be preferred where classical analysis of variance and meta-analysis fail
- Computations are involved (require Markov Chain Monte Carlo method)
- Bayesian inference provides a wealth of information, well beyond GUM requirements
- Classical methods compare well with the Bayesian model proposed, as long as $MS_{\text{between}} > MS_{\text{within}}$