Estimation of between-bottle homogeneity in gas mixtures

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Abstract **In the preparation of synthetic gas mixtures as proficiency testing material, often the between-bottle homogeneity needs be assessed as part of the assignment of reference values to the batch. The existing modelling for between–bottle homogeneity studies is augmented in order to deal with the mathematical particularities of measurements of the complete composition. The estimates obtained for the between-bottle homogeneity and repeatability standard deviation are freed from scatter common to all components, and not caused by effects in the preparation process.**

Introduction

In between-bottle homogeneity studies used in proficiency tests in gas analysis, irregularities are observed in the evaluated between-bottle standard deviation (s_{bb}). In some cases, the s_{bb} of the bulk component appears larger than that of (some of) the minor constituents (table 1).

Table 2: Homogeneity results before normalisation (cmol mol^{-1}) of 4 bottles with natural gas composition

Component	m	s_r	s_{bb}	s_{tot}
Nitrogen	1.30490	0.08%	0.06%	0.10%
Carbon dioxide	0.30240	0.07%	0.12%	0.14%
Methane	87.37260	0.042%	0.032%	0.053%
Ethane	5.98200	0.034%	0.016%	0.038%
Propane	3.00734	0.038%	0.007%	0.039%
Methylpropane	0.48994	0.041%	0.055%	0.068%
Butane	0.47687	0.041%	0.100%	0.108%
Methylbutane	0.47860	0.048%	0.306%	0.31%
Pentane	0.47830	0.045%	0.40%	0.40%
Hexane	0.10717	0.040%	0.87%	0.87%

The aim of this work is to eliminate the irregularity by applying normalisation of the gas composition, as is customary in gas analysis when all components in a mixture are measured. Normalisation eliminates joint effects in the responses of the GC/FID and GC/TCD measurements.

Calibration

The GC is calibrated with 7 mixtures and the results are fitted with a second order polynomial. Due to the fact that all mixtures in the homogeneity study are very close in composition, the conversion from peak area to amount–of–substance fraction can be performed with the same response factors for all mixtures.

The uncertainty associated with the reference values is obtained by duly propagating the uncertainties using the law of propagation of uncertainty. The correlations are appreciated in the uncertainty evaluation.

Normalised homogeneity data

Some examples of the normalisation of data are shown in figures 1 and 2. An overview over all characteristics of the between-bottle homogeneity study data are given in table 2.

Table 2: Homogeneity results after normalisation (cmol mol^{-1})

Component	m	s_r	s_{bb}	s_{tot}
Nitrogen	1.30490	0.07%	0.09%	0.12%
Carbon dioxide	0.30240	0.07%	0.13%	0.15%
Methane	87.37253	0.003%	0.008%	0.008%
Ethane	5.98200	0.020%	0.010%	0.022%
Propane	3.00730	0.015%	0.012%	0.019%
Methylpropane	0.48994	0.016%	0.067%	0.068%
Butane	0.47687	0.015%	0.11%	0.11%
Methylbutane	0.47860	0.021%	0.32%	0.32%
Pentane	0.47830	0.019%	0.41%	0.41%
Hexane	0.10717	0.019%	0.88%	0.88%

Homogeneity data

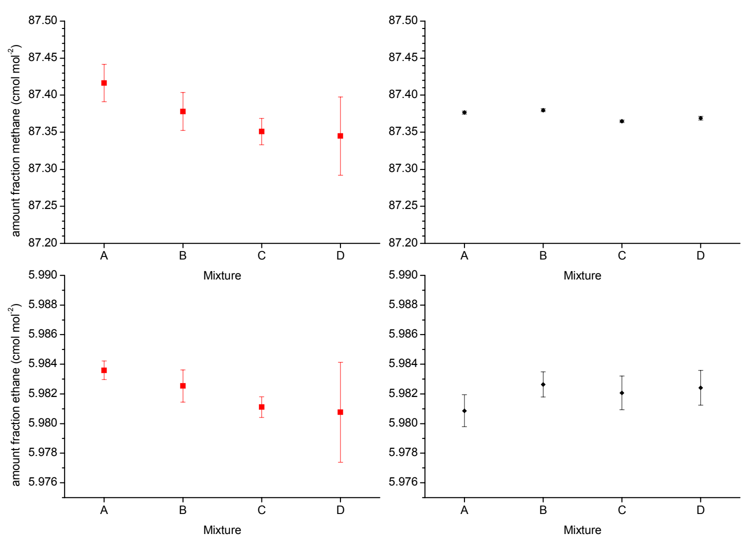

Figure 2: Results before (left) and after (right) normalisation for methane and ethane

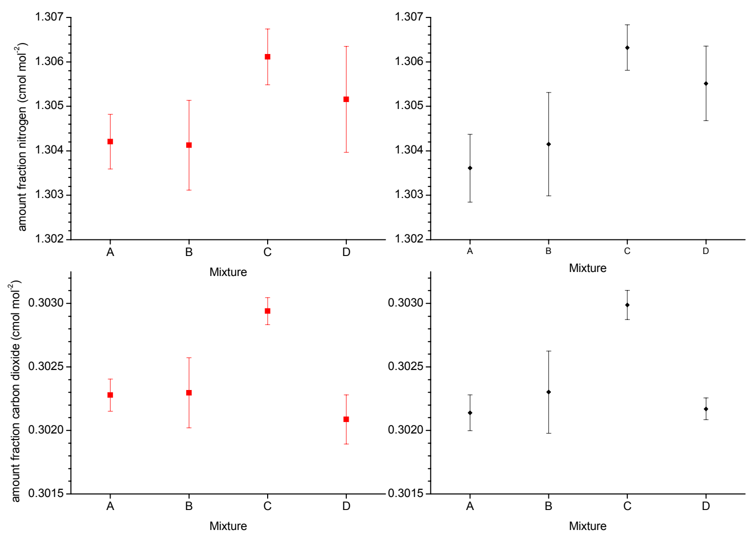

Figure 2: Results before (left) and after (right) normalisation for nitrogen and carbon dioxide

Conclusions

The work shows that it pays of removing joint effects in analytical data to arrive at more realistic values for the batch homogeneity of gas mixtures, thus reducing substantially the uncertainty associated with the reference values for the composition.

VSL is part of the Holland Metrology group. This work was supported by the Dutch Ministry of Economic Affairs.

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