

Harmonisation of coupled calibration curves to reduce correlated effects in the analysis of natural gas by gas chromatography

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Received 30 July 2004; received in revised form 5 November 2004; accepted 10 November 2004

Available online 8 December 2004

Abstract

Quantitative analysis of natural gas depends on the calibration of a gas chromatograph with certified gas mixtures and the determination of a response relationship for each species by regression analysis. The uncertainty in this calibration is dominated by variations in the amount of the sample used for each analysis that are strongly correlated for all species measured in the same run. The “harmonisation” method described here minimises the influence of these correlations on the calculated calibration curves and leads to a reduction in the root-mean-square residual deviations from the fitted curve of a factor between 2 and 5. Consequently, it removes the requirement for each run in the calibration procedure to be carried out under the same external conditions, and opens the possibility that new data, measured under different environmental or instrumental conditions, can be appended to an existing calibration database.

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Keywords: Uncertainty; Normalisation; Harmonisation; Covariance; Correlation; Natural gas; Gases

1. Introduction

Gas chromatography is widely used to measure the composition of natural gas [1]. A feature of this method is that several components in the same sample are analysed simultaneously with different chromatographic columns and detectors. The composition of the complete mixture is then established by combining the results for each component.

The relationship between the response of the gas chromatograph (GC) and the amount fractions certified for a set of standards is related by a calibration curve [2]. This curve is calculated by regression of the measured areas of the peaks detected by the GC against the certified values of the standards. In the case of an analysis of a sample with many components, such as natural gas, a calibration curve is derived independently for each component. This derivation is usually carried out by regression using an ordinary least squares method. Alternatively, a generalised least squares method that takes correct account of the uncertainties associated with

the standards as well as with the analytical data [3] can be used.

One of the largest sources of uncertainty in this type of analysis results from variations in the amount of gas injected into the GC. These variations are referred to as “sample size” variations and are strongly correlated with ambient conditions, particularly ambient pressure, the temperature of the sampling loop, and sample flow. Additionally, some changes in instrumental conditions, such as those leading to changes in the detector gain, can cause variations in the apparent sample size. We refer to all of these as sample size variations because they are common to all components measured during the same analytical run. Consequently, correlated responses are observed for the different gas components that are measured in the same run. It is good practice to design GC hardware to bring such variations within reasonable tolerances, for example by measuring the ambient pressure and using it to correct the response of the GC for resulting variations in sample size. Unfortunately, this is only a partial solution since, for example, it takes no account of sample size variations caused by changes in the sample temperature or the sensitivity of the detectors.

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In this work, we consider a model-based least squares method that compensates for these correlated variations. It reduces the uncertainty associated with the calibration curve by eliminating non-random components. We apply the new “harmonisation” method to a set of calibration data derived from 25 certified mixtures of synthetic natural gas.

The method of harmonisation described here is different from the normalisation method discussed elsewhere [4,5]. That method involves the normalisation of the results to a “complete mixture” (such that the sum of the amount fractions is unity). It is applied to the results of an analysis and corrects them for differences in conditions between the analysis and calibration steps. It works by attributing any difference between the sum of the measured amount fractions and unity to changes in the sample size between the calibrations and the analysis. However, it cannot allow for variations during the calibration process itself. The harmonisation method considered here is applied to the calibration curve and corrects for changes in environmental and instrumental conditions during the calibration process. Additionally, it does not require all components to have been measured, which is a requirement for the normalisation process.

In the following section, we introduce a mathematical analysis of the causes of variations in the sample size in gas chromatography. This analysis justifies the use of an ordinary least squares model for developing the calibration curve. We then introduce the principle of harmonisation of the data using multiplicative correction factors. The performance of the harmonisation method is demonstrated in an un-weighted form. We then show how a weighted approach can be beneficial in some applications.

2. Experimental

The harmonisation method developed here was applied to the analysis of a set of synthetic natural gas mixtures each containing the eleven components listed in Table 1. The amount fractions of all the components in each mix-

Table 1
Range of amount fractions contained in the reference gases studied in this work

Component	Amount fraction (mmol/mol)	
	Minimum	Maximum
Nitrogen	8.08	254
Carbon dioxide	3.41	136
Methane	5.62	971
Ethane	7.26	151
Propane	2.32	75.9
Isobutane	0.36	12.7
<i>n</i> -Butane	0.35	12.7
Neopentane	0.042	3.56
Isopentane	0.084	4.55
<i>n</i> -Pentane	0.085	4.61
<i>n</i> -Hexane	0.037	4.38

ture were known from gravimetric data derived during their preparation [6] and may have uncertainties of 0.002% (relative to value) for the most abundant components and 0.01% for the least abundant. Five components were measured using a thermal-conductivity detector (TCD) with a column of length 4.4 m and internal diameter 0.75 mm packed with Haysep A (120–140 mesh) operated at 160 °C. Seven components were measured with a flame-ionisation detector (FID) and a column operated at the same temperature with the same dimensions packed with Porapak PS (100–120 mesh). Propane was measured with both detectors.

3. Analysis of data

3.1. Model for sample size variations

Suppose we carry out a calibration with N standard gas mixtures, each of which includes a total of Q components. During the analysis of standard mixture j , the amount (n_{ij}) of component i introduced into the GC from the sample loop can be calculated by use of the ideal gas law:

$$n_{ij} = \frac{p_j V}{T_j R} x_{ij}, \quad (1)$$

where p_j is the pressure of the gas in the sample loop and T_j is its temperature at the time of the analysis, V is the volume of the sample loop and R is the ideal gas constant. (It is possible to introduce the compressibility of the mixture into the denominator of the right-hand side of (1) to allow for non-ideal gases. Since there is no significant difference between the compressibilities of the gases considered here, it has been omitted.) The amount fraction of component i in standard j is denoted x_{ij} and is defined by

$$x_{ij} = \frac{n_{ij}}{n_j}, \quad (2)$$

where the total amount of all components is

$$n_j = \sum_{i=1}^Q n_{ij}. \quad (3)$$

Throughout this paper we present more general relationships that are valid for any value of q less than or equal to Q . The integrated area (y_{ij}) recorded by the detector in response to component i in standard j is

$$y_{ij} = r_i n_{ij} \quad (4)$$

where r_i is the relative response factor for the detector to component i . Expression (4) assumes that the detector has a proportional response. In some cases there may be some non-linearity in the response of the detector, in which case a quadratic term can be introduced. Substituting expression (4) into expression (1) leads to the measurement equation for

this process:

$$y_{ij} = r_i \frac{p_j V}{T_j R} x_{ij}. \quad (5)$$

3.2. Formulation of calibration curves using an ordinary least squares model

In line with the conventional approach to developing a calibration curve for each component i , we would fit the model equation

$$y_{ij} = \alpha_i + \beta_i x_{ij} + \eta_{ij} \quad (6)$$

to the measured data by linear regression, where η_{ij} represents an effect presumed to be random and α_j allows for any offset in the detector output during analysis j . The use of this approach assumes that all uncertainties are associated with the y_{ij} and therefore those associated with the x_{ij} are negligible. Since the objective of this work is to develop a calibration curve that can be used to determine the value of an unknown, we fit an “inverse calibration” model of the form:

$$x_{ij} = a_i + b_i y_{ij} + e_{ij} \quad (7)$$

by minimising the sum of the squares of the residual deviations $\sum_{i,j} (x_{ij} - \hat{x}_{ij})^2$, where x is the measured value and \hat{x} the corresponding modelled value. The use of this inverse calibration model is valid when any quadratic component in the response of the detector is small.

3.3. Covariance between the calibration curves

An example of a calibration curve developed for methane using inverse calibration is shown in Fig. 1. The deviations from the fitted line are not readily visible on the scale of the graph; consequently, we analyse the residual deviations defined by $(x - \hat{x})$. These residual deviations from the fitted lines for methane and propane are shown in Figs. 2 and 3.

The extent of correlation in the data can be quantified by evaluating the covariance of the residual deviations from the fitted line. It is convenient to evaluate the covariance with

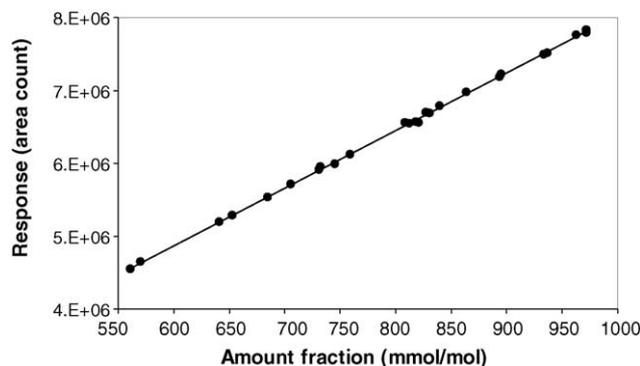


Fig. 1. Calibration data and calibration line for measurements of methane (measured with the TCD). This line was calculated using an ordinary least squares fit to the measurements of methane (area counts) in all 25 standards.

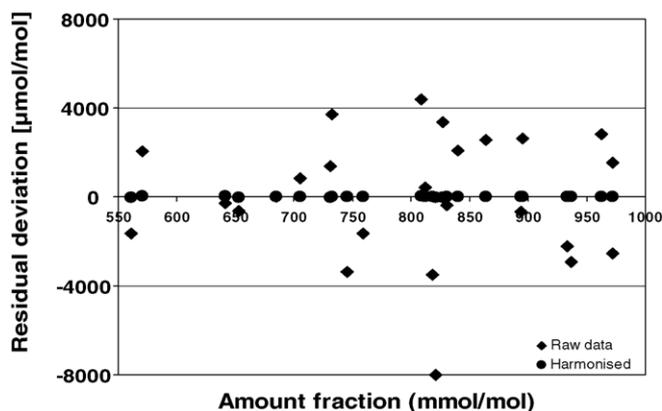


Fig. 2. Residual deviations from the fitted calibration line for methane.

respect to propane, which is measured on both detectors. We use the correlation coefficient [7] of component i defined by

$$\rho_i = \sum_{j=1}^N \frac{x_{ij} - \hat{x}_{ij}}{\text{S.D.}(x_{ij} - \hat{x}_{ij})} \frac{x_{pj} - \hat{x}_{pj}}{\text{S.D.}(x_{pj} - \hat{x}_{pj})}, \quad (8)$$

where x_{ij} is defined as above and x_{pj} is the measured area for propane. The circumflexed quantities are the fitted values using the OLS procedure and $\text{S.D.}(x)$ indicates the standard deviation of x . The results are shown in Table 2.

The residual deviations from the fitted lines are positively correlated with respect to propane for all of the different components in each standard. The correlation is retained for measurements made with the TCD and the FID. These correlations are due to changes in environmental and instrumental conditions (e.g. ambient pressure or temperature of the sampling loop) between the measurement of each standard which affect the amount of substance injected (n_{ij}).

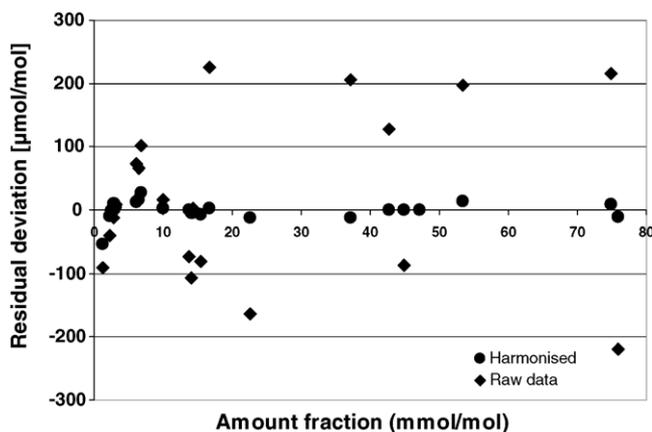


Fig. 3. As Fig. 2 except for propane (measured with the FID).

Table 2
Correlation coefficients for the residual deviations from the fitted curve for each species according to Eq. (8) for the un-weighted fit

Detector	Species	Correlation coefficient	
		Raw data	After harmonisation
TCD	Nitrogen	0.37	−0.05
	Methane	0.63	−0.03
	Carbon dioxide	0.49	0.15
	Ethane	0.83	0.36
FID	Isobutane	0.35	−0.39
	<i>n</i> -Butane	0.52	−0.62
	Neopentane	0.25	−0.75
	Isopentane	0.26	−0.68
	<i>n</i> -Pentane	0.38	−0.58
	<i>n</i> -Hexane	0.11	−0.44

The values for the TCD and the FID data sets are both calculated with respect to propane measured on that detector; hence no value is given for propane.

4. Harmonisation

4.1. Multiplicative model

The principal objective of the harmonisation method described here is to remove the non-random effect from the measured data and hence to improve the fit of the calibration curves to the data. The method compensates for the systematic contribution to the residual deviations from the fitted lines and leads to a corrected set of measurement responses with the covariation reduced.

The harmonisation method is based on the use of a set of multiplicative correction factors c_j that compensate for variations in ambient and instrumental conditions by correcting the ratio p_j/T_j experienced during the analysis of standard j to “standard” conditions p_0/T_0 defined by

$$c_j \frac{p_j}{T_j} = \frac{p_0}{T_0}. \quad (9)$$

Substitution of expression (9) into Eq. (5) leads to a modified measurement equation:

$$y_{ij} = \frac{r_i}{c_j} \frac{p_0 V}{T_0 R} x_{ij}. \quad (10)$$

Table 3
As Table 2 but for the weighted fit

Detector	Species	Correlation coefficient	
		Raw data	After harmonisation
TCD	Nitrogen	0.55	−0.60
	Methane	0.73	−0.18
	Carbon dioxide	0.57	0.00
	Ethane	0.85	0.20
FID	Isobutane	0.34	−0.76
	<i>n</i> -Butane	0.65	−0.72
	Neopentane	0.17	−0.05
	Isopentane	0.26	0.04
	<i>n</i> -Pentane	0.37	0.05
	<i>n</i> -Hexane	−0.01	−0.15

Although the c_j are shown in expression (9) as factors that are multiplied by the ratio of the pressure to the temperature, they also implicitly account for any other multiplicative effect including, for example, detector sensitivity changes. The harmonisation method provides a mathematical basis for calculating the optimum set of c_j .

The modified measurement equation can be re-arranged into the form

$$x_{ij} = \frac{1}{r_i} \frac{T_0 R}{p_0 V} c_j y_{ij}. \quad (11)$$

This form of the modified measurement equation mixes the errors in the c_j with those in y_{ij} and r_i . Our studies show that this does not cause any significant difficulty in the examples considered here [8]. A modified regression model equation can now be fitted to the measured data

$$\hat{x}_{ij} = \hat{a}_i + \hat{b}_i c_j \hat{y}_{ij} + \hat{d}_i (c_j \hat{y}_{ij})^2 + \varepsilon_{ij}, \quad (12)$$

where ε_{ij} is a normally-distributed random variable with zero mean. This modified model equation differs from the model (7) by the introduction of the correction factors c_j on the right-hand side and a quadratic term to model a quadratic deviation from linearity in the response of the detector.

For reasons given elsewhere [8], obtaining a physically feasible least squares solution to this model requires the introduction of a constraint. In the examples presented here, the constraint used is

$$\sum_{j=1}^N c_j = N. \quad (13)$$

The incorporation of this constraint is equivalent to imposing the requirement that the standard conditions (p_0/T_0) to which all measurements are corrected are the mean of all the measurement conditions:

$$\frac{p_0}{T_0} = \frac{1}{N} \sum_{j=1}^N \frac{p_j}{T_j}. \quad (14)$$

4.2. Un-weighted method

The performance of the new method has been tested by developing calibration curves for the data from the 25 standards indicated above. The responses from the two detectors were treated independently by splitting the data into FID ($Q=7$) and TCD ($Q=5$) sets. (Although both detectors measured propane, the response to propane was not used to relate their results by “bridging”.)

Fig. 2 shows the residual deviations ($x_i - \hat{x}_i$) from the fitted lines for methane measured with the TCD before and after the use of the harmonisation method. Similarly, Fig. 3 shows the residual deviations for propane, measured with the FID. In both cases, it is clear that the residual deviations from the fitted line are substantially reduced by the new method.

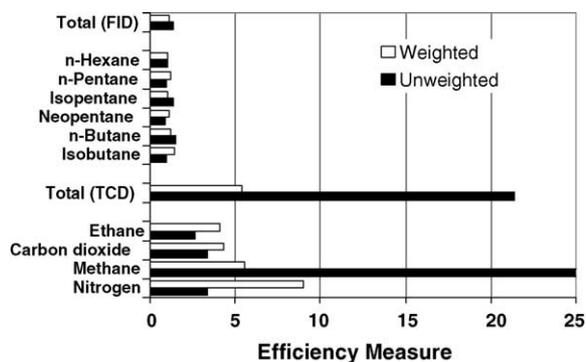


Fig. 4. Efficiency of the harmonisation process measured by the ratio of the residual sum of squares before and after harmonisation (Eq. (15)). The shaded bars indicate the un-weighted fit and the open bars indicate the weighted fit. The efficiency for methane using the un-weighted fit is 136.

A measure of the mean improvement in the residual standard deviation from the fitted model is given by

$$I = \sqrt{\frac{\text{RSS}_{\text{exper}}}{\text{RSS}_{\text{corr}}}}, \quad (15)$$

where ($\text{RSS}_{\text{exper}}$) is the residual sum of squares of the experimental data and (RSS_{corr}) is the residual sum of squares after carrying out the harmonisation. The quantity I is also equal to the ratio of the standard deviations of the residual deviations with and without harmonisation. Consequently, it can be considered to be a measure of the reduction in the uncertainty of the measurements [9]. Expression (15) can be applied to the residual sum of squares for each component and also to the total for all components. Fig. 4 shows the calculated values for each component as well as for all components. We see that the method is most efficient in improving the fit of the TCD data to the model for methane ($I=136$) and the FID data for propane ($I=9.5$). The reason for these particular improvements is that the amount fractions, and hence the residual deviations for methane and propane are much larger (see Table 1). This is a consequence of solving the set of models for each component i by minimising the sum of the ε_{ij}^2 for that i .

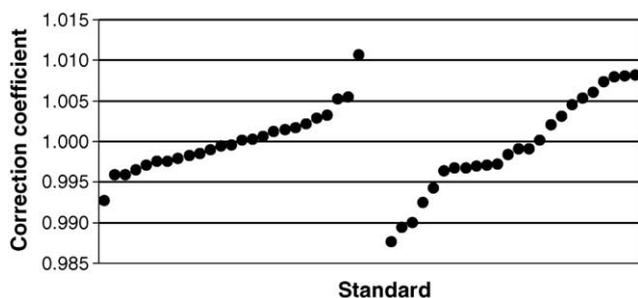


Fig. 5. Values for the correction coefficients (c_j) for the 25 standards. For clarity, the values have been plotted in ascending order. The series on the left were measured with the TCD and the series on the right with the FID.

Fig. 5 shows the values of the set of correction coefficients (c_j) for the TCD and FID data. The only explicit requirement on the c_j is that their mean is unity (following the constraint (13)). The corrections for the TCD are in the range $\pm 1.1\%$ (of value). The spread of the c_j is larger for the FID ($\pm 1.5\%$ of value) because it is generally more subject to environmental and instrumental influences.

The data in Table 2 show how the correlation coefficients for the results for each component (formula (8)) have been changed by the application of the harmonisation method. As described in Section 3.3, the correlation coefficients for all components in the raw data are positive, which confirms the presence of sources of correlated variation across the data. When the TCD data has been processed, the positive correlations are decreased or removed. In contrast, the correlations in the FID data are increased and change sign (from correlation to anti-correlation). This indicates the tendency of this method, in its un-weighted implementation (as shown in the previous section), to “over-fit” the data because of the presence of a single component at a much higher concentration.

4.3. Weighted method

An alternative approach that has the potential to balance the improvement more evenly amongst the components is to solve the modified measurement model (Eq. (12)) by minimising the sum of the weighted deviations given by $\sum_{i,j} (1 - \hat{x}_{ij}/x_{ij})^2$. An example of the results of such a weighted fit for methane and propane is shown in Figs. 6 and 7, which can be compared with Figs. 2 and 3. The residuals for the data after application of the new method are larger for both methane and propane because the use of the weighting has reduced the tendency of the method to “over-fit” the data to the most abundant component.

The efficiencies for each component for the weighted and un-weighted methods are shown in Fig. 4. The improvement for methane is reduced from 136 to 5.6 and propane from 9.5

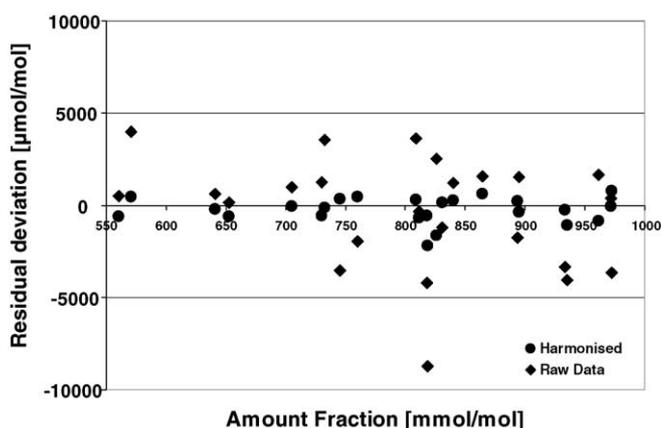


Fig. 6. Residual deviations from the fitted calibration line for methane for the weighted fit.

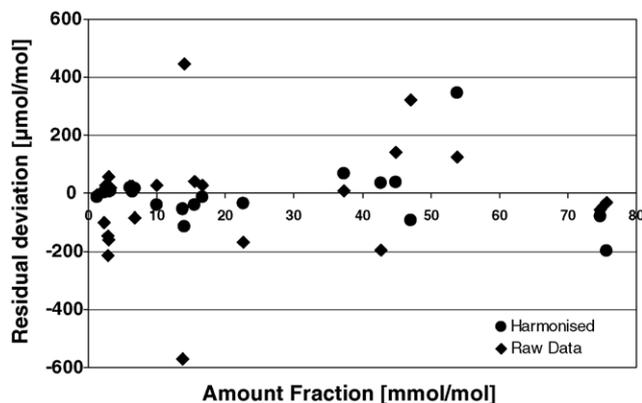


Fig. 7. As Fig. 6 except for propane (measured with the FID).

to 2.6. The reduction in improvement for methane leads to a reduction in the overall improvement for the TCD data. The total efficiency is almost unchanged for the FID data. The change in the FID data is less significant because the ratio of the concentration of propane to the other components is not as large as the corresponding ratio for methane in the TCD data and because there are more random sources of variation present.

The correlation coefficients for the weighted fits are shown in Table 3. It can be seen that the weighted method does not have the same tendency to “over-fit” the most abundant components and is generally more effective in reducing the correlation in the other components. The increase in the correlation coefficient for nitrogen reflects the fact that the correlation coefficient measures the fraction of the residual variation that is correlated. In this case, the residual variation is reduced, but the fraction of it that is correlated is increased. The use of the weighted method changes the set of correction coefficients (c_i) for both detectors by less than 0.05% from those for the un-weighted approach. This is because the extent of the environmental effects are not influenced by the type of fitting method used, which largely influences the values of the fitted coefficients.

4.4. Inverse calibration

The objective of establishing a calibration curve is generally to make use of it for the analysis of an unknown. This is often called the “inverse calibration” step. Since the new method reduces the uncertainty in the set of calibration curves by achieving a better fit to all the data simultaneously, it can be expected to reduce the uncertainty in the inverse calibration step.

The constant coefficients \hat{a}_i of the fitted calibration curves for the raw data change by less than 0.1% when the harmonisation method (either with or without weighting) is used. The change for methane is approximately 1%, which is a consequence of the limited dynamic range of the methane data, which are within less than a factor of two in amount fraction. Hence, the fitted curve “pivots” around the cluster of data,

leading to large changes in the intercept, but with limited influence on the results of the inverse calibration.

5. Conclusions

A new method for the reduction in correlated variations in coupled calibration curves has been described. It leads to a substantial reduction in the residual deviations from the calibration line by removing correlated effects from the data. The method can be extended to apply to polynomial curves, weighted least-squares and generalised least-squares methods. The harmonisation method presented here is applicable to any set of data with two or more channels of information that contain mutual dependencies.

We have presented an example of the application of the method to the development of calibration curves for the eleven components in a set of synthetic natural gas mixtures. It has more effect in reducing the uncertainty associated with the higher concentration components measured on the TCD than the lower concentration components measured on the FID because they are less subject to random variations. It has the advantages over normalisation methods [4] that it is applied to the calibration curve itself and it does not require all compounds present to be quantified. Hence, it can be used with or without a “bridging” compound to link sets of data acquired with different columns.

In this application, the new method has the advantage that it does not require all the measurements to be acquired rapidly in order to maintain constant environmental and instrumental conditions. It can also be used in such a way that the curve can be updated when new data become available, even when environmental or instrumental conditions have changed. A particular example of the application of the new method is when it is necessary to verify the values of a synthetic standard gas mixture by analysis. In general, it is good practice for the calibration curve to be developed at the same time as the analysis. The use of the harmonisation method enables such an analysis to be carried out with reduced uncertainty and without the constraint that the analysis and the calibration are carried out under the same instrumental and environmental conditions.

Acknowledgements

This work was supported by the UK Department of Trade and Industry under the National Measurement System’s Valid Analytical Measurement (VAM) programme. The authors acknowledge useful discussions with Andrew Brown.

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