



Paper 28: 5.2

EVALUATION OF ON-LINE CHROMATOGRAPH PERFORMANCE

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SUMMARY

Gas Chromatography (GC) is very widely used for analysis of natural gas, with the most frequent use for the analytical data being the calculation of properties of the gas. Just as the composition data are used to calculate properties, so the uncertainty values associated with the composition data allow calculation of the uncertainty associated with the property. International Standard ISO 10723 [1] describes the procedures for estimation of composition uncertainty. This paper describes the use of ISO 10723, the range of results found, and the influence of these results on the calculated Calorific Value (CV) of natural gases. Similar calculations can be applied to other properties.

INTRODUCTION

Analysis of natural gas by gas chromatography is a well-established and mature technology. The most common configuration allows analysis of N₂, CO₂, C₁ to C₅ hydrocarbons individually, and a composite C₆+, representing all hydrocarbons of carbon number 6 and above. The particular chromatographic requirements of natural gas mean that the C₃ to C₅ hydrocarbons are separated on one column, which has a short pre-section from which C₆+ is backflushed, while the N₂, CO₂, C₁ and C₂ are stored in a separate column more suitable to their needs, and separated later in the analytical run. A further column may be introduced to allow separation and measurement of both O₂ and N₂. This is more common for laboratory-based analysers; on-line process instruments are very unlikely to be subject to air contamination.

Although the arrangement sounds complicated, the switching events occur under automatic control, and once set up, the chromatographic conditions are very stable. Analysis times are typically in the range 5 to 20 minutes. Other instrument configurations are available, including the use of a temperature-programmed capillary column for details of the higher hydrocarbons. For most properties, however, with the exception of hydrocarbon dewpoint and related calculations, analysis to C₆+ is sufficient.

PERFORMANCE EVALUATION

ISO 10723, "Natural gas - Performance evaluation for on-line analytical systems" was written so as not to be technique specific, other than to assume that the method of analysis produces composition data. Test gases are introduced, and the resulting data evaluated. To date, it has only been applied to gas chromatographs, but if a new and competitive analytical method emerges in the future, it should be equally applicable. Although the name suggests on-line systems, it can be and has been used successfully with laboratory analysers.

The evaluation procedure gives quantitative uncertainty values which will arise from the use of the analyser under defined conditions. It is assumed that the user has a set of requirements which the analyser is meant to satisfy. These should include

- ◆ The range of components to be analysed (normally decided before purchase).
- ◆ The range of compositions for each component.
- ◆ The allowable uncertainty for component measurement and/or calculated properties.

The procedure then covers the following topics in the context of the user's requirements:

- ◆ Is the instrument fit for purpose?
 - properly configured for natural gas analysis
 - measuring the range of components required
- ◆ Is it efficient?
 - separating components without them interfering with each other
 - completing the analysis in an acceptable time
- ◆ Is it precise?
 - capable of producing repeatable data when analysing a single gas
 - does repeatability vary with component concentration?
- ◆ Do bias errors arise from non-linear response?

The first two headings cover characteristics which are mainly answered by inspection, although whether it covers the concentration ranges required will arise from the testing. Error measurement is derived from the use of test gases.

Errors can be categorised as being either random or systematic (bias errors). Random errors arise because no system is capable of producing exactly the same data output when the same operations (analyses) are performed. In natural gas analysis by GC, typical causes of random errors include variations and spikes in the electrical supply, electrical interference from other equipment, changes in ambient conditions, particularly barometric pressure, and variations in operator procedure. Precision statements are the normal way of quantifying random error. Systematic errors can arise from improperly configured systems which fail to measure some components, from errors in the calibration gas being used, and from false assumptions about the nature of the instrument response characteristics. (This last cause is typically due to the assumption that the response/concentration relationship is a straight line through the origin, whereas in fact it follows a curve).

The procedure requires the use of seven test gases, so that each component is measured at seven different concentrations. These should cover a range slightly greater than that for which the analyser is required, and ideally be more or less equally spaced across that range. Given these requirements, the mixtures will have unusual compositions, and must be prepared according to the application. The gases need not contain all components, but should as a minimum contain N₂, CO₂, C₁, C₂, C₃ and C₄.

The test gases are each analysed several times, so as to get repeatability data at the different component concentrations. The analysis cycle time usually dictates how many repeats are possible at each level; all analyses should be completed during a single calibration interval,

typically a working day. With faster analysers, six to eight repeats can be achieved for each gas in half a day. More than this number of repeats is not really necessary.

Figure 1 illustrates a set of results for one component. The precision is evaluated from the scatter of results at each concentration, and the response curve is fitted to the mean values at each concentration.

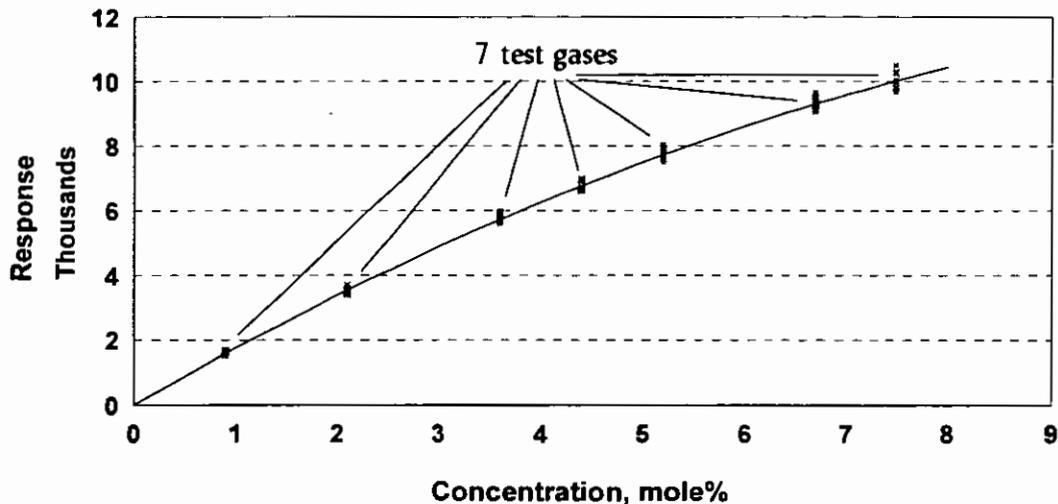


Figure 1. Use of test gases

The data are inspected for outliers before being subjected to regression analysis. This allows the precision for each component to be expressed either as a function of concentration or as a uniform value across the range, and the response curve to be expressed as a first-, second- or third-order polynomial.

PRECISION

Significance of Precision data

The standard deviation of a set of repeat data is easy to express, but by itself does not allow random error calculation which is meaningful. If we assume that:

- samples are measured by an analyser of known precision which uses a certified calibration mixture as a working standard on a day to day basis,
- the working standard has itself been measured against a primary, for example gravimetric, calibration standard, using an analyser with comparable precision to that used for sample measurement,
- both the primary and certified calibration mixtures are of similar composition to the sample, and
- the uncertainties associated with the composition of the primary calibration standard are small,

then we can create an error budget. The concentration, x_{iws} , of component i in the certified working standard is expressed as

$$x_{iws} = \frac{x_{ipr} \times A_{iws}}{A_{ipr}} \quad (1)$$

where x_{ipr} is the concentration of component i in the primary calibration standard
 A_{iws} is the analyser response to component i in the working standard
 A_{ipr} is the analyser response to component i in the primary calibration standard.

The concentration of component i in the sample, x_{isam} , is calculated as

$$x_{isam} = \frac{x_{iws} \times A_{isam}}{A_{iws}} \quad (2)$$

where A_{isam} is the analyser response to component i in the sample.

Combining these equations,

$$x_{isam} = \frac{x_{ipr} \times A_{iws} \times A_{isam}}{A_{ipr} \times A_{iws}} \quad (3)$$

Although A_{iws} , which appears in both the numerator and the denominator of equation (3), can be cancelled out when calculating the concentration, this is not permitted for statistical treatment of uncertainty. The uncertainty in x_{isam} , δx_{isam} , is expressed as

$$\frac{\delta x_{isam}}{x_{isam}} = \sqrt{\left(\frac{\delta x_{ipr}}{x_{ipr}}\right)^2 + 2 \times \left(\frac{\delta A_{iws}}{A_{iws}}\right)^2 + \left(\frac{\delta A_{isam}}{A_{isam}}\right)^2 + \left(\frac{\delta A_{ipr}}{A_{ipr}}\right)^2} \quad (4)$$

where δabc is the uncertainty in abc .

Equation 4 gives the random uncertainty for a component which has been analysed as described. According to ISO 6976 [2] the uncertainty on calculated CV, δH_{mix}^0 , can be derived from the individual component uncertainties by

$$\delta H_{mix}^0 = \sqrt{\sum_{i=1}^N [\delta x_i \times (H_i^0 - H_{mix}^0)]^2} \quad (5)$$

Equation 5 sums the individual component uncertainties to give a CV uncertainty. Because it works this way, if the analytical requirement is to achieve a defined uncertainty on calculated CV, there is not a reverse route which will allow calculation of the component uncertainties from a required CV uncertainty. In the same way, a calculated CV alone does not allow the composition from which it was derived to be deduced.

Because a defined property uncertainty is a common requirement, we studied the precision data from a large number of process GCs to see if there is a useable relationship between property and component uncertainty. Figure 2 illustrates the data.

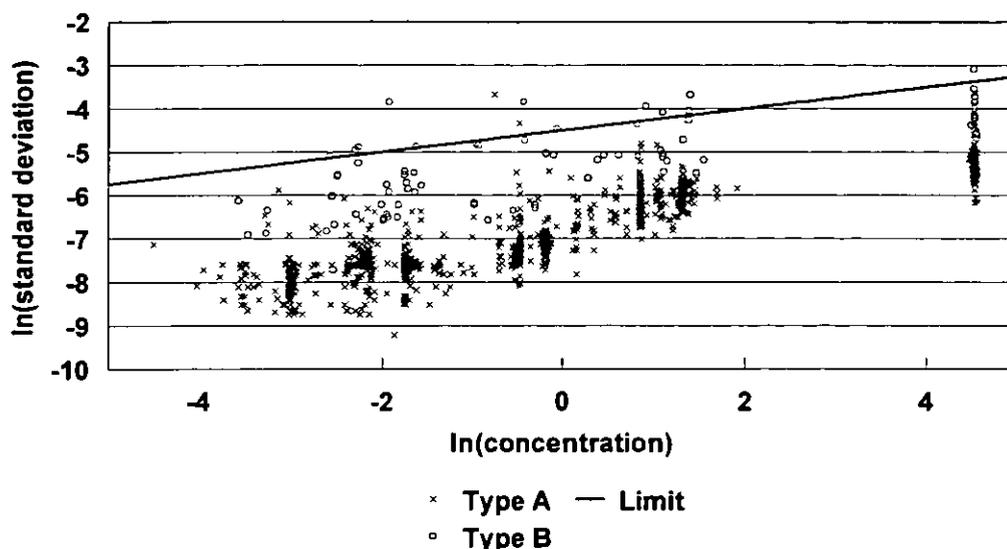


Figure 2. Relationship between standard deviation and concentration

When plotting standard deviations against concentration for different components which cover similar concentration ranges (for example N_2 and C_2), we found that concentration had more effect than the nature of the component. Their precision was linked more to the concentration, and broadly independent of what they were. Extending this to all components, expressed as natural logarithms to recognise the concentration differences, we found that the relationship extends over the entire component range. Furthermore, plotting data from instruments from two sources (Type A and B in Figure 2) shows that the precision of each type is different. Each shows a mean behaviour, expressed as

$$\ln(\text{standard deviation}) = A + B * \ln(\text{concentration})$$

with different coefficients A and B for each type.

It is possible to draw a line (Limit in Figure 2) which acts as a boundary to almost all the observations, and which has the equation

$$\ln(\text{standard deviation}) = -4.5 + 0.25 * \ln(\text{concentration}). \quad (6)$$

Applying these values to give an overall component uncertainty according to equation 4, and hence, for a series of typical natural gases, a CV uncertainty according to equation 5 gives values of slightly less than 0.1 MJ/m^3 . In other words, if the requirement were for a method which would give a calculated CV with an uncertainty of 0.1 MJ/m^3 , or approximately 0.25% relative, then any analyser where component standard deviations are shown to be below the limit value of equation 6 will satisfy the requirement.

Application of precision data

Since the composition and related uncertainties of a natural gas control the calculated CV and its uncertainty, respectively, it is of interest to study the effect of differing compositions and levels of precision. Five natural gas compositions were considered. One was a typical North Sea gas, and the other four were taken from an American Petroleum Institute group on

sampling [3]. These latter were formulated to represent CVs expressed in BTU of 800, 1000, 1250 and 1500. Such gases have wide compositional variations, and are chosen as deliberate extremes, to illustrate the effects.

Three levels of precision were considered. The best was taken from the mean values for Type A analysers illustrated in Figure 2. The boundary values from equation 6 were used for the "average" case, and the final values were taken from the worst case which we have encountered. The resulting CV uncertainties are listed in Table 1 and illustrated in Figure 3.

Table 1. CV uncertainty derived from component random errors

	Calorific Value	Calorific Value uncertainty MJ/m ³		
		Mean Type A	Limit	Worst case
North Sea gas	38.91	0.017	0.095	0.140
800 BTU gas	29.87	0.056	0.187	0.195
1000 BTU gas	37.36	0.012	0.081	0.114
1250 BTU gas	46.63	0.058	0.135	0.231
1500 BTU gas	55.98	0.187	0.242	0.372

From Table 1, it is clear that the best precision applies to the North Sea and 1000 BTU gases. For the other gases, the error increases according to how far their CVs differ from that of methane. The reason is implicit in equation 5. Gases with CVs close to that of methane tend to contain methane at the 90% level. In this case, the methane uncertainty makes very little contribution, as its CV is close to that of the mixture, and the sum of the contributing components is relatively small.

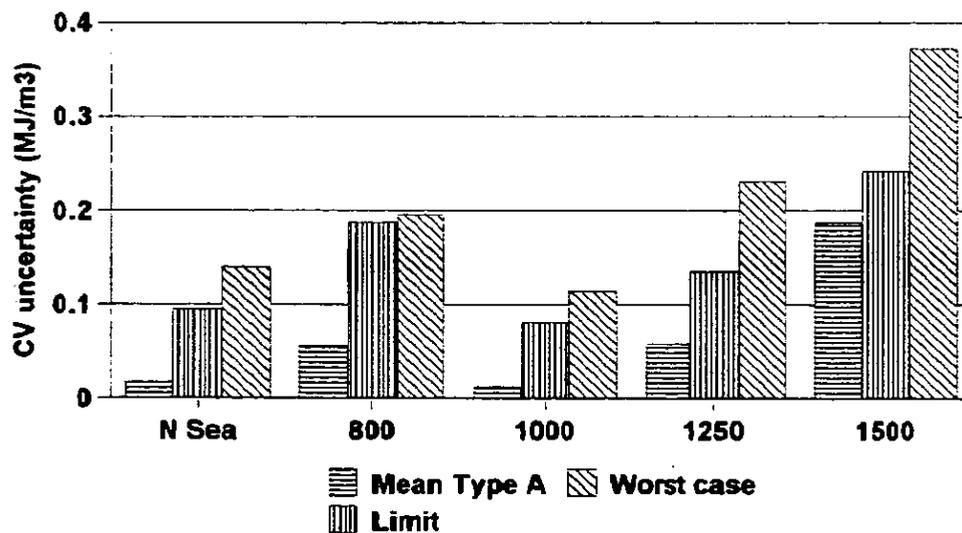


Figure 3. CV uncertainty derived from component random errors

With the best component precision (Mean Type A), there is a large difference in CV uncertainty according to composition (greater than a factor of 10). With the Limit precision,

only the high methane gases have CV uncertainty less than 0.1 MJ/m^3 , and none of the gases in the Worst Case. These last figures would be good reason to reject an instrument. The Limit values can thus be seen to be appropriate for high methane gases, and if a CV uncertainty of 0.1 MJ/m^3 is required for other compositions, a more stringent component precision would be required.

BIAS ERRORS

Significance of bias errors

For the purpose of this paper, we assume that there is no bias error associated with the calibration gas, and that such error derives from deviations from response linearity, under circumstances where the data handling procedures assume that all components show fully linear response. It is possible, by multi-level calibration, to recognise and allow for non-linear response, but it is not the usual practice. We are only considering analyser response, because a faulty calibration gas is easily replaced, whereas an analyser is not.

Non-linearity of response is illustrated in Figure 4.

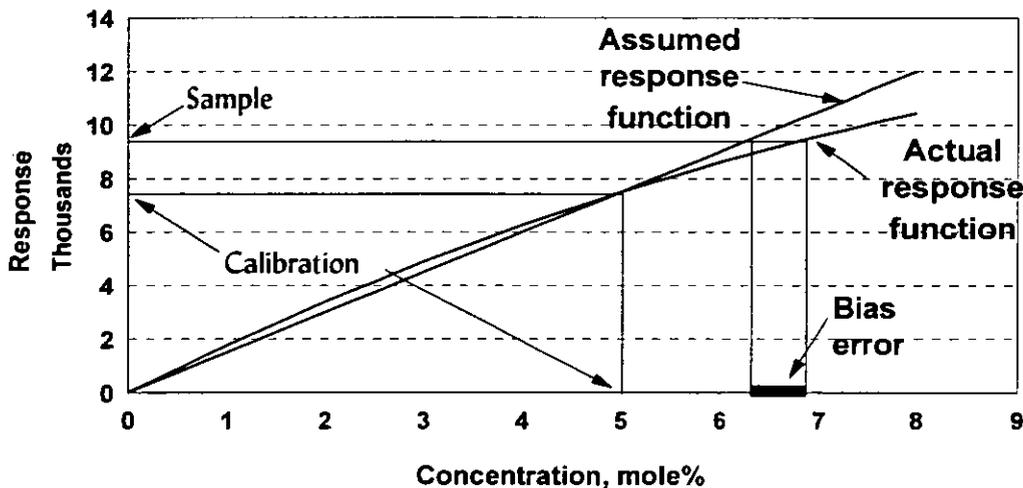


Figure 4. Bias error due to non-linearity

Bias errors only arise when the analyser is calibrated with a gas whose composition is significantly different from that of the sample. If they are effectively the same, or very similar, they will be using the same part of the response curve, and its shape does not matter, except that the response should increase with increasing component concentration. The circumstances described in the previous section, where the primary calibration gas, the certified daily calibration gas and the sample had very similar concentrations, would not give rise to significant bias error. We are not always so fortunate, however, and sample differences can cause problems.

The bias error for a component i depends upon the measured (f_i) and assumed (g_i) response functions, and upon the component concentrations in the calibration gas ($x_{i, \text{std}}$) and the sample ($x_{i, \text{sample}}$), according to

$$\text{Error}_i = g_i^{-1} \times \left[\frac{g_i(x_{\text{istd}}) \times f_i(x_{\text{isample}})}{f_i(x_{\text{istd}})} \right] - x_{\text{isample}}$$

The error tends to zero as the function f_i and g_i converge, or as the concentrations x_{istd} and x_{isample} converge. Bias errors are either positive or negative, as opposed to random errors, which define an uncertainty area about the "true" value. They can therefore reinforce or cancel each other's contribution to a property. Thus a positive bias error for nitrogen will reduce the resulting CV; a similar positive error for ethane will increase the CV, largely cancelling the effect of nitrogen.

Application of bias errors

The fact that bias errors are positive or negative means that it is more difficult to generalise about their effects. The following calculations use the same five compositions described above, with each being used in turn as calibration gas for analysis of the others. The measured response function is taken from the typical behaviour of a Type A analyser, and the assumed response function is complete linearity, i.e. a straight line through the origin. The resulting CV errors are listed in Table 2 and illustrated in Figures 5 and 6

Table 2. CV bias derived from component bias errors

Calibration gas	Sample gas				
	CV bias error - MJ/m ³				
	N. Sea gas	800 BTU	1000 BTU	1250 BTU	1500 BTU
N. Sea gas	0	0.540	-0.002	-0.112	-0.277
800 BTU	-0.014	0	-0.037	-0.018	-0.143
1000 BTU	0.005	0.556	0	-0.094	-0.275
1250 BTU	0.021	0.476	-0.003	0	-0.157
1500 BTU	0.021	0.385	-0.015	0.091	0

Figure 5 illustrates the CV bias as a function of the calibration gas, and Figure 6 as a function of the sample gas.

For the North Sea and the 1000 BTU gases, the bias error in each case is small when compared to a typical CV uncertainty requirement of 0.1 MJ/m³. In such a case, the bias error is small enough to be ignored - it would be lost in the random uncertainty noise associated with the calculated CV. For the other gases, particularly the 800 and 1500 BTU gases, the bias error is significant and (probably) unacceptable. The solution in this case would be to choose an analyser with a more favourable response function, or, more simply, to choose a calibration gas closer in composition to, and hence better adapted for that type of sample.

It is interesting to note that the bias depends more upon the sample than upon the calibration gas. Figure 6 shows more closely consistent sets of bias errors when categorised according to the sample, and by far the lowest bias when the sample is a high methane gas. This can be explained intuitively. If the sample gas were pure methane, then the nature of the calibration

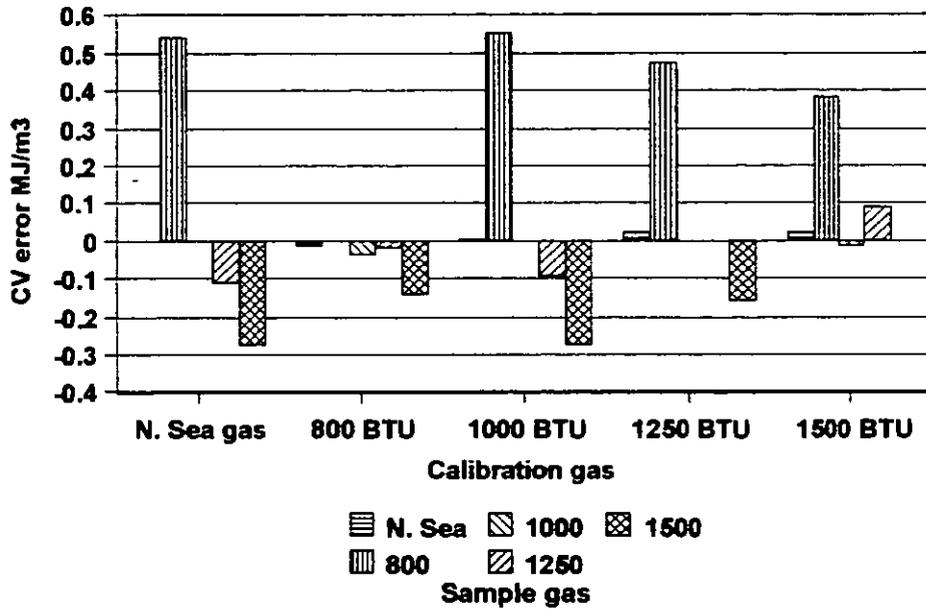


Figure 5. CV bias as a function of calibration gas

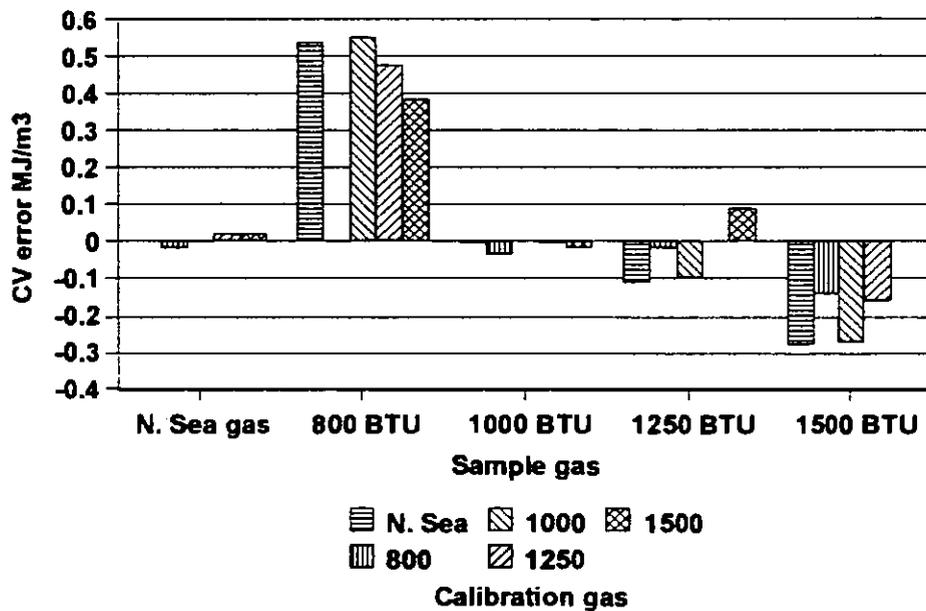


Figure 6. CV bias as a function of sample gas

gas is unimportant. Bias errors resulting from different calibration gas compositions would cause the measured methane in the sample to be different from 100%, but in the absence of any other measured components, normalisation would return the value to 100%. The further the sample composition deviates from pure methane, the greater the potential for bias errors to be significant.

It is unwise to generalise about the size of bias errors. If the North Sea gas is used as a calibration mixture for analysis of the 1500 BTU gas, the resulting bias error would be -0.277 MJ/m^3 . If their roles were reversed, the bias would be 0.021 MJ/m^3 .

ALTERNATIVE PROCEDURE

The use of seven test gases is not always practically convenient. Offshore operations are an obvious case in point. We have therefore considered and tested an alternative approach, using injection of a single gas at different pressures to simulate gases of different compositions. Figure 7 illustrates this approach.

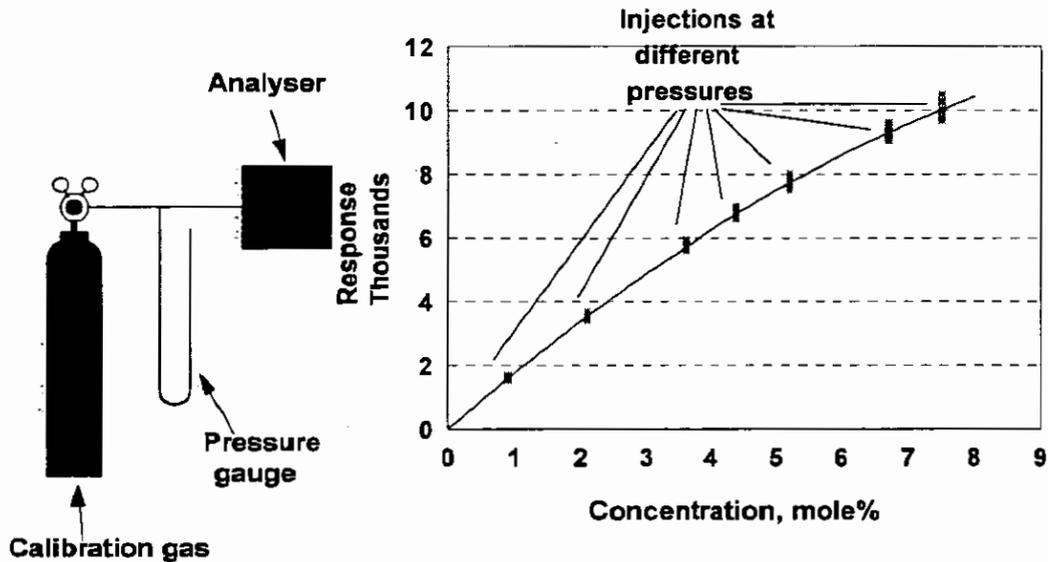


Figure 7. Variable pressure injection

The best choice for the single gas to be used is the existing calibration gas, which should have been chosen to be compatible with the expected sample compositions. Apart from convenience, an interesting feature is that the accuracy requirement for the test procedure is transferred from the seven test mixtures to the means of pressure measurement. Calculations show that the inherent accuracy of the evaluation procedure remains comparable, whichever procedure is followed.

CONCLUSIONS

ISO 10723 offers a procedure for natural gas analyser evaluation which quantifies the uncertainty of component measurement. The resulting data can be used directly, for product allocation, for example, or to compute properties such as CV, in which case the property uncertainty can be derived from the component data. Regular application of this procedure (for example, annually) would ensure that the user has an up to date certificate which describes the analyser's performance. With such a certificate, the user can confidently demonstrate that the analyser's contribution to, for example, fiscal metering is satisfactory.

An alternative approach, whereby instead of seven test gases, a single gas is used at a range of pressures, has been assessed and shown to be satisfactory.

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