ADVANCES IN ON-LINE GAS CHROMATOGRAPHY IN THE NATURAL GAS INDUSTRY

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1   INTRODUCTION

On line gas chromatography has been used in the natural gas industry for many years, principally as a means of determining composition for calorific value calculation. Advances in such diverse areas as microprocessor electronics and calibration gas preparation now allow the existing chromatograph technology to be utilised for more accurate and sophisticated measurements. Techniques that once could only be implemented in the laboratory can now be routinely used in the field. This paper discusses:

- Improved accuracy by use of multipoint calibration
- Potential dual detector applications
- Determination of hydrocarbon dew-point from on-line analysis

2   IMPROVED ACCURACY BY MULTI-POINT CALIBRATION

Natural gas is a complex mixture of hydrocarbons and permanent gases. For physical property determination all components from methane to hexanes and above, nitrogen and carbon dioxide have to be measured. Component concentrations can vary from 100 ppm or less for hexanes and pentanes to 95 % or more for methane, giving a dynamic range of almost 10^5.

Traditionally most analytical systems have assumed the following relationship between detector response and component concentration:

$$R = X_i \cdot c \tag{1}$$

This is the equation of a straight line through the origin and justifies single point calibration, as only the constant needs to be defined [1]. In practice it has long been known that this straight line relationship between response and concentration is an approximation, especially for major components such as methane. Furthermore, the approximation only holds well when the sample analysed is of a similar composition to the calibration standard. Indeed, ISO6974 (1984) [2] recommended maximum limits for the difference between calibration gas concentrations and line gas concentrations.

Theoretically at least, a more accurate analysis can be obtained by determining the true nature of the response concentration relationship and using this in data processing calculations. Therefore, given that ISO 6974 was published in 1984 the question arises as to why has the assumption still continued to be used on many analytical systems? The answer to this can be given in three parts

First, there have until recently, been no agreed international standards which cover multi-point calibration or related issues [3].

Second, use of the straight line relationship has many attractions. It is conceptually straightforward. Calculation of component concentrations is easy to execute in a field instrument, although this is less of a problem now with the current availability of micro-proCessors. Only a single point calibration is necessary, i.e., only one calibration gas is required and the technique is simple to implement and validate. Furthermore, when natural gas analysers are measuring gas from a single source the range of measurement may be such that any non-linearity errors are small relative to other errors in the system.

Third, negative arguments have been made against multi-point calibration, i.e., it is complex and its implementation is time consuming. Moreover, that the benefits gained in analytical accuracy do not justify the efforts involved. Finally, because of the complexity of the process the calibration of the instrument will not be checked frequently.   However, these objections can now be overcome:

From a practical point of view the implementation of multi-point calibration does require a certain amount of effort and expense. Several high accuracy, gravimetrically prepared, test gases are required. Complex calculations must be implemented in the data processing programme of the analyser. A consistent, ideally automated, system must be developed to run the test gases and determine the response concentration relationships. All of this can be done, however, the cost and effort, for a chromatograph manufacturer is only justifiable when a large number of analysers are involved.

Once this initial work has been done, the implementation of the technique in the factory or laboratory is relatively straightforward. The gases, covering the full range of expected concentrations for all major components (C_1 to C, N_2 and CO_2), be analysed using an automated test rig. Response concentration functions are calculated and checked to be third order or less, typically first or second order fits are obtained. Finally, a set of known gases are analysed and the values of physical properties are checked to be within 0.1 % of the certified values for calorific value and density.

2.1   Benefits of Multi-Point Calibration

The question of benefit of this technique, that is increased accuracy, can now be considered. If the natural gas to be analysed is coming from a source where the concentrations of individual components are relatively stable, e.g., the UK North Sea, then a single point calibration will normally give acceptably small errors in physical property measurement. However, increasingly, pipeline gases come from a variety of sources with widely different component concentrations. When a wide range of gas compositions have to be measured component concentrations cannot all be near the calibration point. The further away any single calibration point is from the measured value the more likely it is that the response function calculated from the single point calibration is incorrect. Thus, the single point calibration method becomes less accurate. The data presented in figure one shows a comparison of differences between measured and certified values for an MPC calibrated and a single point calibrated analyser.

Figure 1: Comparison of results of MPC and non MPC calibration on PTB test gases

Comparision of MPC and non MPC GC
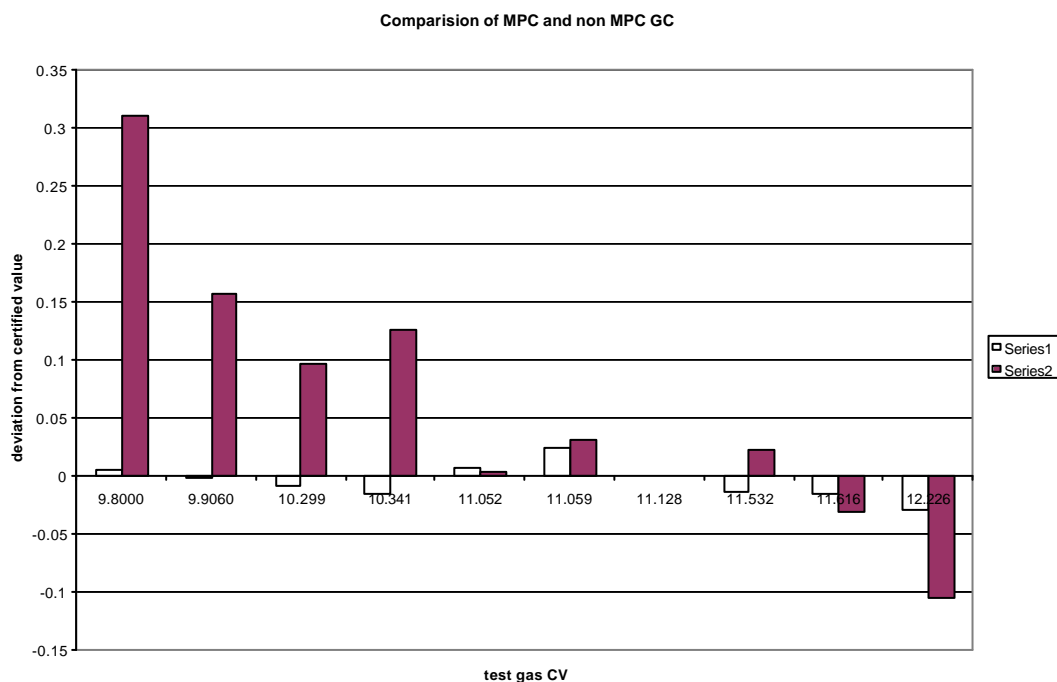
Clearly, there is a benefit in using multi-point calibration.

2.2   Multi-Point Calibration In The Field

For multi-point calibration to be implemented in a field unit two further key questions arise. First can it be made to work on a day to day basis and second what is its long term performance?

It has already been noted that because of its very nature multi-point calibration cannot be repeated frequently. Furthermore, any field analyser, whatever its calibration method, must have a stable response/concentration relationship. Nevertheless, a regular check is usually required to confirm analyser performance, provide an audit trail point and if necessary make any small adjustments for day to day fluctuations. With a single point calibrated instrument this involves a new calibration and acceptance of new response factors providing they are within a pre-set limit of the last valid calibration. For a multipoint calibrated instrument a similar procedure is used. A single calibration gas is analysed to check that the calibration is still valid by calculating a response factor:

$$Rf = \frac{aP^3 + bP^2 + cP + d}{Xic} \tag{2}$$

The value of this response factor should be close to one and deviations from one beyond a preset range can be used to cause a calibration alarm in the same way as for single point calibration.

The response factors are then used to calculate component concentrations in the sample gas:

$$Xis \quad \% = \frac{aP^3 + bP2^3 + cP + d}{Rf} \tag{3}$$

Full details of the calculation are given in elsewhere [4].

It is a matter of good practice that the performance of field analysers should be assessed on a regular basis, typically, a one year interval is used. Part of this assessment must be a check on the validity of the calibration and with multi-point calibration there are two obvious options. Standard test gases can be analysed and the results checked to be within the required accuracy or not. Alternatively, the calibration can be repeated and a new set of response concentration curves determined. Which method is chosen will depend on the end user of the instrument.

Daniel uses checking a set of known standards as part of its multi-point calibration procedure. For a group of analysers installed on a particular transmission system this check is also used on a one or two yearly basis to confirm that the calibration is still valid. Physical properties of four test gases are determined. If the required accuracy of physical property measurement is not achieved for all of the test gases then the instrument must be re-calibrated. Measurements of calorific values, without re-calibration and taken two years apart, for two types of standard gas on one analyser are shown in Table 1.

Table 1 - Test Gas Analysis Results of GCs Installed on a Transmission System

	Actual CV (MJm^{-3})	Measured CV (MJm^{-3})	% difference	Pass/fail
1997	**35.106**	**35.117**	**0.031**	**Pass**
	40.290	**40.277**	**(0.032)**	**Pass**
1999	**35.109**	**35.119**	**0.027**	**Pass**
	40.290	**40.280**	**(0.026)**	**Pass**

This unit was originally multi-point calibrated in 1996 and the data demonstrates that once an instrument has been multi-point calibrated it can maintain its performance in the field over several years. Furthermore, of twenty five analysers installed in 1996 and checked by Daniel every year since not one has been re-calibrated. Therefore, multi-point calibration can be implemented for on-line analysers in a transmission system.

3   DUAL DETECTOR METHODS

Advances in gas chromatograph controller hardware and software now make it possible to install additional sample valves and detectors. This allows simultaneous dual methods analysis to be carried out on any given stream. Dual detector methods can be used to analyse components that are difficult to measure because of constraints of carrier gas, chromatographic separation, sensitivity or time. For example dual detector systems can facilitate

- extended analysis of components previously backflushed,
- simultaneous measurement of hydrogen or helium utilising a nitrogen carrier gas and a second detector
- measurement of trace hydrogen sulphide down to 2 ppm.

One of these methods will now be discussed in detail.

3.1   Extended Analysis to C9+

Traditionally, single detector systems have been used to analyse up to C6+. That is, all hydrocarbon components above pentanes are measured as a single composite component peak. Physical properties are then calculated from an assigned breakdown of this C6+ fraction into C6, C7, and C8 components, either in the chromatograph controller or in a system flow computer.

Typically, transmission gases contain up to C9 or C10 hydrocarbons [4] and a dual detector system has been developed which performs an extended analysis to C9+, with C10+ currently being investigated. In this system the first detector is configured for measurement of components from methane to pentanes, nitrogen and carbon dioxide. The second detector measures hexanes through nonanes. Results from both detectors are combined in post analysis calculations.

To simplify operation the second detector is calibrated with normal components as response factors within a carbon number grouping are similar.

Figure 2 - Calibration Gas Chromatogram of C6 to C8 Components

C9+ calibration gas - C6 to C8
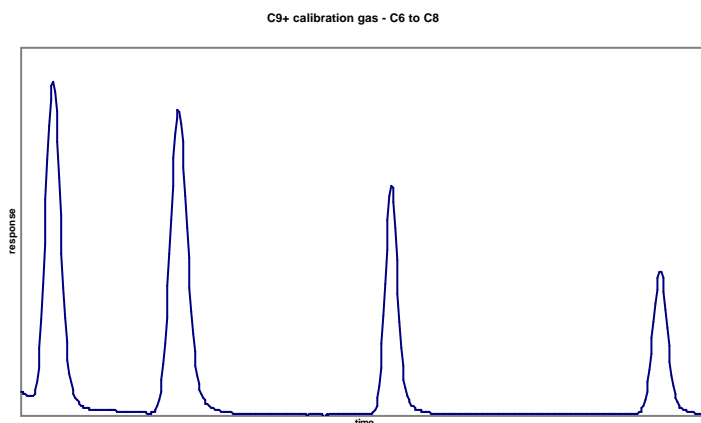
Real natural gases contain many isomers other than the straight chain normal components. Analysis on the second detector is by carbon number grouping and, with the normal isomers providing gating peaks for identification and integration.

Figure 3 - Natural Gas Chromatogram of C6 to C8 Components

C9+ natural gas - C6 to C8
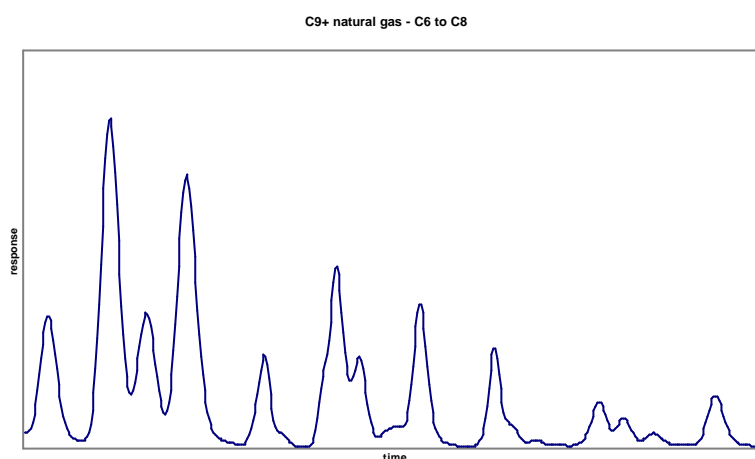
Recent results indicate that the minimum measurable quantity for a C9+ component is below 2 ppm, indicating detailed information on the composition of the natural gas in question can be obtained.

The advantages of this approach are that components C6 to C9+ used in calculations such as AGA 8 super-copressibility, can be directly measured rather than approximated. Use of dual detectors allows greatly reduced time for the analysis and increased sensitivity for the minor components. Furthermore, for hydrocarbon rich gases the full contributions of the heavier components to CV and density can be determined.

The principle difficulties are associated with calibration of the C6 to C9+ measurement. First, obtaining a suitable calibration gas with acceptable composition and uncertainties. Second, any calibration gas containing significant quantities of C6 and above components will have to be supplied at low pressure to avoid dew-point problems or be maintained at specific temperature. Currently the use of pentanes as a bridging component to allow relative response factors for C6 and above to be used is being investigated.

4   DETERMINATION OF HYDROCARBON DEWPOINT FROM ANALYSIS

Calculations of hydrocarbon dew-point from compositional data are well established. Furthermore, gas chromatography is the accepted method of performing gas analysis. It has already been noted that transmission gases typically contain hydrocarbons only up to C9 or C10. Moreover, ppm analytical sensitivity for these components can be obtained. Therefore, a combination of extended on-line analysis and a suitable calculation gives the possibility of hydrocarbon dewpoint determination.

4.1   Calculations.

Hydrocarbon dewpoint calculations based on two empirically derived equations of state, PR [5] and RKS [6],[7], have been implemented in a GC controller. At present, there are no internationally recognised standards defining how hydrocarbon dew-point should be calculated, therefore, the controller calculations have been checked against and existing desktop package (GasVLE).

Results from each calculation compare favourably and generally the difference is small (less than 0.5ºC). Divergence only starts to occur at high pressures in the region of the dew-line, where the rate of change of dew temperature with pressure is very high and never exceeded 2 °C. The generally accepted accuracy of hydrocarbon dew-point calculated from analysis is +/- 2°C. This is significantly greater than the differences observed and from this it can be concluded that the GC controller calculations are valid. Figure 4 shows corresponding dew-lines calculated from the desktop and GC controller packages, which are almost co-incident.

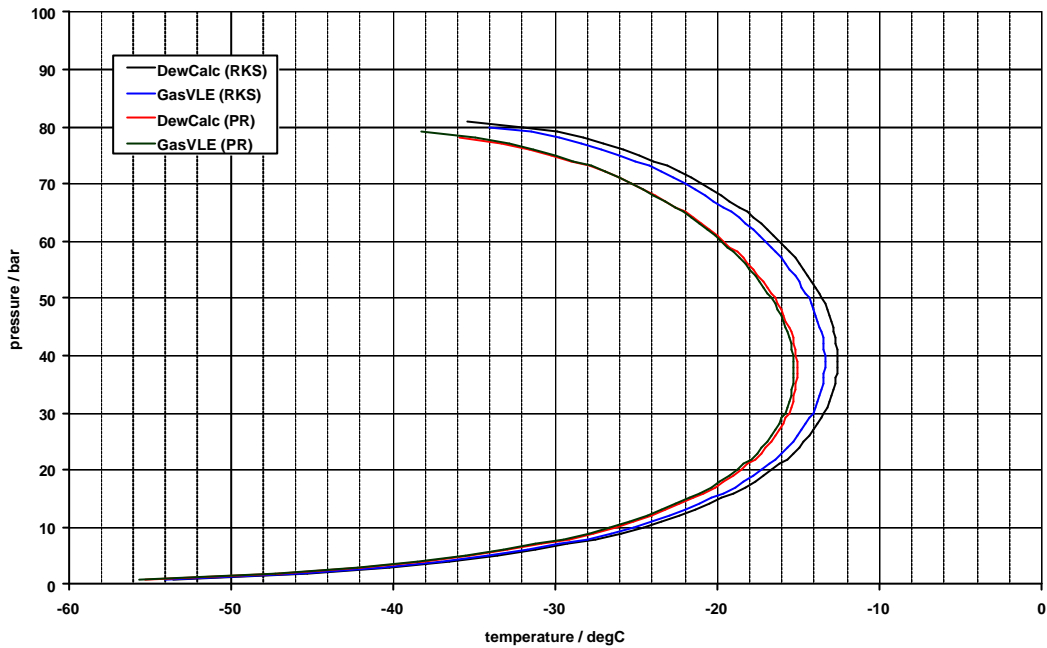Figure 4 – Comparison of Dewlines From Desktop and GC Controller Calculations

Figure 5 more clearly shows the small differences between the calculated values, which are to be expected as the calculations use different source data. The differences remain insignificant until the cricondentherm is approached.

Figure 5 – Differences of Calculation Results Between Desktop Package and GC Controller

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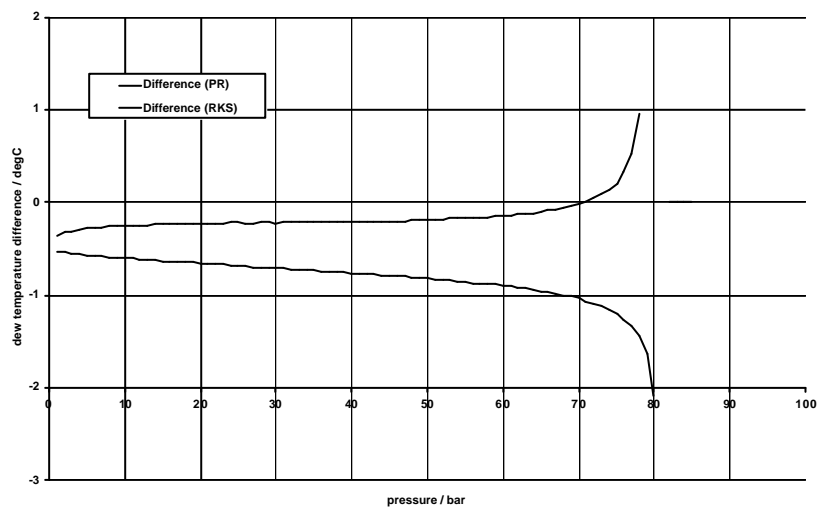
4.2   Carbon Number Group Properties

Physical properties such as calorific value or density vary little within a carbon number grouping.   Therefore, for these standard properties, values associated with the normal component can be assigned to all isomers of the same carbon number for calculation purposes. Unfortunately, this approach is not valid for hydrocarbon dewpoint calculation; the normal component is the highest boiling point isomer and hydrocarbon dew-point calculation based on normal component properties will lead to an over estimation of the dew temperature. For a typical North Sea gas this over estimation can be greater than $10^{o}C$ [8].

It is not practicable to provide an on line measurement of every isomer between C6 and C9. Nevertheless, it is known that isomer ratios within a carbon number grouping are relatively constant.   Thus, detailed composition can be determined of line, in a laboratory, and breakdown values entered into the process unit. The breakdown data should be updated on a regular basis. Irrespective of the accuracy of the breakdown data an on-line calculation will provide a valuable tracking tool.

4.3   Analytical Performance

Analysis of a C9+ calibration gas gave calculated hydrocarbon dew-point repeatably to +/- $0.2\ ^{o}C$. Such precision is essential in order to identify real changes in gas hydrocarbon dew-point.

Small changes in higher hydrocarbon components have a proportionally greater effect on hydrocarbon dew-point that lower carbon number components in a typical natural gas. As a rough rule of thumb, a change in C9 concentration of 1ppm can be thought of as causing a $0.5^{o}C$ change in dewpoint temperature, whereas an 8 ppm change in C7 concatenation would be required to produce the same effect. With an analytical sensitivity to 1 ppm or less changes in C9+ concentrations, combined with the observed repeatability, detection of dew point changes of $1^{o}C$ are possible.   Furthermore, minimum detectable quantity of approximately 2 ppm indicates that relatively low hydrocarbon dew-points can be determined.

5   CONCLUSIONS

In conclusion, three main points can be taken from Daniel's experience with multi-point calibration:

• First, the practical challenges of multi-point calibration can be overcome.

• Second, when a wide range of gas compositions have to be measured multi-point calibration gives increased analytical accuracy and hence increased physical property measurement accuracy.

• Third, once calibrated, the performance of field units is maintained over several years without re-calibration.

The use of dual detector systems gives the opportunity to use current technology to perform a much wider range of analyses and gain significantly more information on the overall gas quality.

• Extended analysis off natural gas on a dual detector system allows direct measurement of all components used in heating value and compressibility calculations.

• Hydrocarbon dewpoint can be calculated repeatably from a C9+ analysis and small changes in the process gas can be detected.   This offers a valuable tool for tracking dewpoint. With correct calibration and use of extended analysis data a means of accurately determining hydrocarbon dewpoint can be obtained.

6   NOTATION

R	**Detector response**
RFi	response factor for component i
a, b, c, d	constants
Xic	concentration of component i in calibration gas
Xis	concentration of component i in sample gas

7   REFERENCES

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[3]   ISO 6974 (2000) – Natural gas – Determination of composition with defined uncertainty by gas chromatography.

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