



# Analysis of natural gas: the necessity of multiple standards for calibration

George C. Rhoderick\*

*Analytical Chemistry Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology,  
Building 227/B120, 100 Bureau Drive Gaithersburg, MD 20899 USA*

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## Abstract

The importance of natural gas as an international trading commodity and the cost to consumers has made the accuracy of determinations for the components of natural gas very important. Pricing of natural gas is based on the heating value of the gas determined from either calorimetry measurements or calculations based on individual component concentrations determined by gas chromatography (GC). Due to the expense of accurate calibration standards, many analysts and laboratories will use a single calibration standard to perform natural gas determinations. Therefore, the purpose of this study was to determine whether an analyst could accurately measure the components of natural gas, in particular methane, using a single standard, or whether a suite of standards is necessary to calibrate the analytical instrument. A suite of eight gravimetric primary standards was prepared covering a concentration range for methane of 64–94 mol%, with uncertainties of  $\pm 0.05\%$  relative (95% confidence interval). These natural gas primary standards also contained nitrogen, carbon dioxide, ethane, propane, *iso*-butane, *n*-butane, *iso*-pentane, *n*-pentane, and *n*-hexane with varying concentrations from 0.02 to 14%. A single analytical method was used in which only the amount of sample injected onto the column was altered. The results show that when injecting a 0.5 ml sample volume a second-order regression through the standards is necessary for the determination of methane. The results for nitrogen, ethane and propane also show the same trend. Only those individual standards whose methane concentration is within 1% of the test mixture predicted a concentration within 0.05% of the regression value. Those individual primary standards whose methane concentration is different by more than  $\pm 1\%$  of the test mixture predicted values differing by  $\pm 0.5$  to  $\pm 2.0\%$  from the regression value. These differences lie well outside the predicted concentration uncertainty interval of  $\pm 0.20\%$ . A smaller sample volume, 0.1 ml, resulted in a set of data that could be fit using linear regression. Each of the eight primary standards individually predicted the methane in the test mixture to be within  $\pm 0.11\%$  of the predicted value from linear regression. The data confirm that it is imperative to fully characterize the analytical system before proceeding with an analysis.

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## 1. Introduction

Natural gas is sold to consumers based on its heating value expressed as joules (or British thermal unit; Btu/ft<sup>3</sup>) [1]. It has also become increasingly important

\* Tel.: +1-301-9753937.

E-mail address: [george.rhoderick@nist.gov](mailto:george.rhoderick@nist.gov) (G.C. Rhoderick).

as a commodity traded internationally. These two features make it very important to accurately know the thermal content of metered gas. Early on, the measurement of physical properties, in particular the calorific value, was done by direct methods such as calorimetry. Gas chromatography (GC) equipped with thermal conductivity and flame-ionization detectors (FID) have become popular for speciation and measurement of natural gas. In this method, the actual concentration of each individual component in the natural gas sample is determined by calibration with reference standards. The heating value for each compound is then calculated using the concentration and heating values for each compound from calorific data [2]. The individual heating values are summed for a total value reported as Btu.

There are many reported methods and accepted procedures being used for natural gas analysis [3–6]. Due to the complex make-up of natural gas, these methods generally require several detectors, multiple columns, and backflushing techniques to achieve precise measurements of all the individual components found in the natural gas. One reported method uses a 3 m × 3.2 mm Poropak T column, as specified in International Organization for Standardization (ISO) 6569 [7], for the separation of nitrogen, carbon dioxide and C<sub>1</sub>–C<sub>4</sub> hydrocarbons. Another author reported using this ISO 6569 method modified with a pre-column and backflushing to analyze the C<sub>5</sub> and C<sub>6</sub> hydrocarbons [8]. The run time upto and including C<sub>6</sub> is about 20 min. Most of the discussion on natural gas in the literature deals with precision and to some extent accuracy. Authors state that they calibrate with gravimetrically prepared standards and mixtures of known content, sometimes using only one standard. However, there are no reports as to the significance of the number of standards used for instrument calibration. A previous paper by this author explored the use of single component versus multi-component standards, i.e. ethane in methane versus all the hydrocarbons of interest. This research was performed to determine if other compounds in the sample had an adverse effect on the determination of a single component in a complex mixture as compared to the determination by a single component standard. That previous research did not address using a suite of standards, each containing the full complement of natural gas components, as opposed to one single standard containing all the

components [9]. Therefore, the objective of this study was to determine if multiple standards are necessary for accurate determinations of natural gas, with special attention to methane. To simplify the analysis a procedure using only one column and thermal conductivity detection (TCD) is used. While not necessarily superior to other analytical procedures which require two separate columns and detectors, it allows for all compounds to be determined using one analytical column and detector.

Those chemists and practitioners in the laboratories must be acutely aware of the possible pitfalls related to the manner in which they calibrate their instrumentation. While this paper addresses mainly calibration standards, the author believes that a much wider audience that deals with chromatography issues will be reached through publication in this journal.

## 2. Experimental

### 2.1. Reagents and gas cylinders

Gas cylinders of pure methane, nitrogen, carbon dioxide, ethane, propane, 2-methylpropane (*iso*-butane) and *n*-butane were obtained with manufacturer claimed purities of >99.5%. Pure liquid samples of 2-methylbutane (*iso*-pentane), *n*-pentane and *n*-hexane were also obtained from a commercial source with claimed purities of >99.5%. The compounds were analyzed at NIST for impurities using GC with flame-ionization detection, thermal conductivity detection and mass spectrometry. In the case of methane, ethane, propane and the butanes the vapor phase was analyzed. To ensure that the composition of the vapor phase did not change during use, the reagent gases were reanalyzed after they were used to prepare the primary gravimetric standards, with no change in composition occurring. Size 3.4 and 6 l aluminum gas cylinders equipped with brass GCA-350 valves were purchased from a specialty gas company. The cylinder manufacturer used a cleaning process and the specialty gas company did further drying and processing.

### 2.2. Primary standards preparation

A suite of eight primary standards was prepared gravimetrically using two different methods—one for

Table 1  
Primary gravimetric standard suite concentration ranges

Component	Primary standards concentration range (% mol/mol)	Test mixture nominal concentrations (% mol/mol)
Nitrogen	1–18	12
Carbon dioxide	1–10	4
Methane	64–95	82
Ethane	0.7–14	0.75
Propane	0.25–6.3	0.30
<i>iso</i> -Butane	0.09–1.4	0.20
<i>n</i> -Butane	0.09–1.4	0.20
<i>iso</i> -Pentane	0.03–0.1	0.05
<i>n</i> -Pentane	0.03–0.1	0.05
<i>n</i> -Hexane	0.02–0.1	0.05

liquids and one for gases. The standards contained nitrogen, carbon dioxide and C<sub>1</sub> through C<sub>6</sub> hydrocarbons. Table 1 lists the compounds and the concentration range of the prepared primary standards suite. The liquid compounds were added to the cylinders via a previously described capillary tube gravimetric technique to produce standards which are known to accurately measure these gaseous species [9]. Empty capillary tubes sealed on one end were weighed using a 100 g capacity balance readable to 0.001 mg. Each liquid hydrocarbon was introduced into individual capillary tubes, the ends sealed and then reweighed. The aluminum cylinder was evacuated and weighed. The liquid hydrocarbons were transferred to the evacuated cylinder via each individual compound capillary tube. The gaseous compounds were added gravimetrically to the cylinders via a gas manifold system, starting with the compound with the lowest vapor pressure. The final compound and major component added was the methane. A two-pan, 10 kg capacity balance with a sensitivity of 0.001 g was used to weigh the gaseous compounds into the 3.4 l cylinders. A 50 kg capacity two-pan balance with a sensitivity of 0.001 g was used to weigh the 6 l cylinders.

### 2.3. Test mixture

A synthetic sample of natural gas was obtained from a specialty gas company with manufacturer-assigned concentrations. It contained the same components as the gravimetric primary standards. The test mixture was used as the control to determine how well the analytical system performed.

### 2.4. Measurement system

All analyses were performed on a Hewlett-Packard 5890 GC<sup>1</sup> equipped with a TCD. A 9.1 m × 0.32 cm stainless steel column packed with 23% SP-1700 on 80/100 mesh support was used to separate the components of the natural gas standards and the test mixture in less than 25 min. The column oven temperature was isothermal at 40 °C for 8 min then temperature programmed to 105 °C at 30 °C/min and held for 15 min. Helium carrier gas flow was set at 18 ml/min with a detector make-up flow of 25 ml/min. The TCD was operated at 150 °C in the low sensitivity mode. Measurements were made using 0.5 and 0.1 ml stainless steel sample loops connected to a six-port stainless steel gas sample valve.

## 3. Results and discussion

Analysis of the suite of gravimetric primary standards and the test mixture (reference standard) were first performed using the 0.5 ml sample loop. The test mixture was used as the control sample, which was sampled before and after each primary standard to monitor instrument function. The analytical sequence for sampling was test mixture, primary standard 1, test mixture, primary standard 2, test mixture, . . . , continued through all eight standards. Each test mixture or primary standard was sampled three times and the area responses averaged. Ratios were determined by dividing the average GC area response for the primary standard by that of the average of the two test mixture averages bracketing the respective primary standard. The data were plotted and fitted to the appropriate regression function. A response factor (RF) was calculated for each primary standard by dividing its respective ratio by the gravimetric concentration. The RFs were used to determine the appropriate regression function to apply. Table 2 lists the ratio, gravimetric concentration, response factor, the predicted

<sup>1</sup> Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 2  
Methane data obtained using 0.5 ml sample loop plotted to second-order regression

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration <sup>b</sup>	Response factor (RF)	Predicted concentration <sup>b</sup>	Difference <sup>c</sup> (%)
X16157	0.8070 ± 0.0009	64.66 ± 0.06	0.01248	64.60 ± 0.16	−0.09
X16140	0.8640 ± 0.0009	69.53 ± 0.07	0.01243	69.58 ± 0.17	0.07
X16136	0.9385 ± 0.0009	76.06 ± 0.08	0.01234	76.19 ± 0.17	0.17
CAL7493	0.9875 ± 0.0009	80.69 ± 0.08	0.01224	80.60 ± 0.16	−0.11
X302429	1.0014 ± 0.0011	81.82 ± 0.08	0.01224	81.87 ± 0.20	0.06
X16106	1.0297 ± 0.0014	84.60 ± 0.08	0.01217	84.48 ± 0.25	−0.14
X16115	1.0974 ± 0.0020	90.67 ± 0.09	0.01210	90.72 ± 0.34	0.06
X16156	1.1373 ± 0.0013	94.46 ± 0.09	0.01204	94.47 ± 0.23	0.01
Test mixture	1.0000 ± 0.0010			81.74 ± 0.20	

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as  $1\sigma$ .

<sup>b</sup> The true concentration of methane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

<sup>c</sup> The difference (%) is calculated from: [(predicted concentration − gravimetric concentration)/gravimetric concentration] × 100.

concentration, and the percent difference between the gravimetric and predicted concentrations for methane. The data show that, with increasing concentration, the RF decreases by  $\approx 5\%$  over the concentration range of the primary standards suite, which covers a 30% spread. This trend indicates that a second-order regression plot would be the most appropriate for this set of data. Using the second-order regression results in percent differences that are well within the uncertainty for each respective primary standard. The concentration of the test sample is then predicted from the regression, resulting in a value of  $81.74 \pm 0.20\%$ . This is a 0.07% relative difference between the NIST predicted value and manufacturer-assigned concentration of 81.68%.

The gravimetric and predicted concentrations for the methane given in Table 2 include a total expanded uncertainty. The total uncertainty of each primary gravimetric standard consists of several sources of errors. Sources include the uncertainty in weighing compounds into the cylinders and the purity of the starting compounds. It is expressed as an expanded uncertainty  $U = ku_c$  with  $u_c$  estimated from the preparation uncertainties and the coverage factor  $k$  equal to 2 (95% confidence interval) [10]. The  $u_c$  portion is calculated using the equation:  $(a^2 + b^2)^{1/2}$ . The true value, with 95% confidence, is expected to lie in the interval defined by the gravimetric value  $\pm$  the expanded uncertainty. The uncertainty for the predicted concentrations of the test mixture using each primary standard includes the gravimetric uncertainty

and the uncertainty in comparing the standards to the test mixture.

Using the same set of data, the methane concentration of the test sample was calculated directly to each of the eight primary standards. The response ratio of the test sample, 1.0000, is divided by that of the primary standard and multiplied by the gravimetric concentration. Table 3 lists the gravimetric concentration of each primary standard, the concentration of the test mixture versus each standard and the percent difference between the assigned test value and that determined from each primary standard. The uncertainty associated with the test mixture concentration includes the uncertainty in the primary standard and the uncertainty in comparing the test mixture to the primary standards (reported at the 95% confidence level). There are two primary standards whose concentrations are within 1% of the assigned value of the test mixture. The resulting concentrations for the test mixture versus these two primary standards are less than 0.1% different from the predicted second-order regression concentration,  $81.74 \pm 0.20 \text{ mol}\%$ , given in Table 2. However, as the primary standard concentrations are displaced farther away from the test mixture, the percent difference between the predicted values from the individual primary standards and the regression value get much larger. These differences are as much as  $\approx 1\%$  using primary standards  $\pm 5\%$  of the concentration of the test mixture and  $\approx 2\%$  at the extreme ends of the standard suite range. These

Table 3  
Methane concentration determined vs. each primary gravimetric standard from 0.5 ml sample loop data

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration (% mol/mol) <sup>b</sup>	Concentration in test mixture vs. primary standard (% mol/mol) <sup>b</sup>	Difference (%) from regression value (81.74% mol/mol)
X16157	0.8070 ± 0.0009	64.66 ± 0.06	80.12 ± 0.19	-2.0
X16140	0.8640 ± 0.0009	69.53 ± 0.06	80.48 ± 0.18	-1.5
X16136	0.9385 ± 0.0009	76.06 ± 0.08	81.04 ± 0.18	-0.9
CAL7493	0.9875 ± 0.0009	80.69 ± 0.08	81.71 ± 0.17	-0.04
X302429	1.0014 ± 0.0011	81.82 ± 0.08	81.70 ± 0.20	-0.05
X16106	1.0297 ± 0.0014	84.60 ± 0.08	82.16 ± 0.25	0.5
X16115	1.0974 ± 0.0020	90.67 ± 0.09	82.62 ± 0.31	1.1
X16156	1.1373 ± 0.0013	94.46 ± 0.09	83.05 ± 0.20	1.6

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as  $1\sigma$ .

<sup>b</sup> The true concentration of methane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

differences are also significantly outside the expanded uncertainty maximum of  $\pm 0.3\%$  of the predicted concentrations. These results are better visualized in Fig. 1. The y-axis represents the percent difference from the predicted concentration from the regression value of the test mixture. Therefore, zero on the y-axis represents the regression value of the test mixture and each data point is the difference from the predicted

regression value. The value next to the data point is the concentration of the primary standard used to determine the methane in the test mixture. The error bars represent the expanded uncertainty in the predicted concentration in the test mixture versus the respective primary standard as listed in Table 3.

Using this analytical procedure, all of the compounds in the natural gas primary standards and test

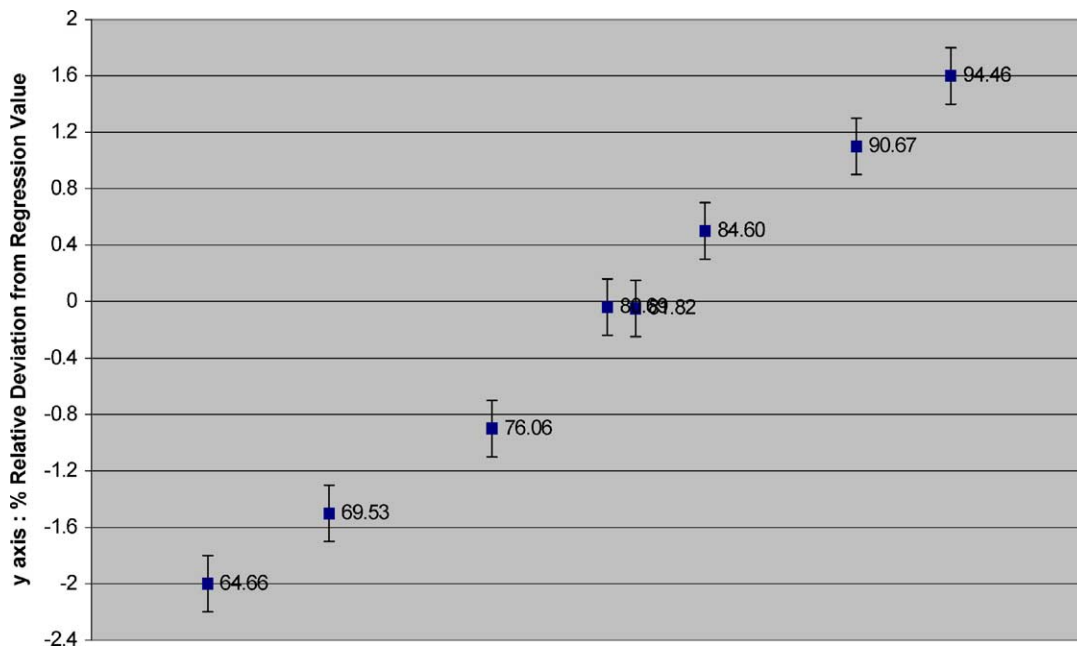


Fig. 1. Comparison of differences of the test mixture between regression value and values by individual primary standards (in % mol/mol).

Table 4  
The *n*-butane data obtained using 0.5 ml sample loop plotted to linear regression

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration <sup>b</sup>	Response factor (RF)	Predicted concentration <sup>b</sup>	Difference <sup>c</sup> (%)
CAL7493	0.4808 ± 0.0021	0.0976 ± 0.0001	4.93	0.0977 ± 0.0009	0.10
X16115	0.5038 ± 0.0022	0.1024 ± 0.0001	4.92	0.1023 ± 0.0009	−0.10
X16156	0.9501 ± 0.0029	0.1925 ± 0.0002	4.94	0.1921 ± 0.0012	−0.20
X16140	1.0002 ± 0.0041	0.2021 ± 0.0002	4.95	0.2022 ± 0.0017	0.05
X16136	1.3940 ± 0.0046	0.2819 ± 0.0003	4.94	0.2815 ± 0.0019	−0.14
X10106	3.973 ± 0.024	0.7973 ± 0.0008	4.98	0.8004 ± 0.0096	0.39
CAL014774	5.002 ± 0.012	1.0101 ± 0.0010	4.95	1.0075 ± 0.0049	−0.26
X16157	7.066 ± 0.032	1.4226 ± 0.0014	4.97	1.423 ± 0.013	0.02
Test mixture	1.0000	0.2022 ± 0.0018			

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as  $1\sigma$ .

<sup>b</sup> The true concentration of *n*-butane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

<sup>c</sup> The difference (%) is calculated from: [(predicted concentration − gravimetric concentration)/gravimetric concentration] × 100.

mixture were detected. The GC area responses for each compound were large enough to result in typically no more than 0.3% standard deviation for at least three replicate injections of a single standard. Results for nitrogen, ethane and propane show the same trend. However, due to the large amount of data generated, those compounds will not be further discussed. Data for each of the other hydrocarbons and carbon dioxide were such that linear regression was used to determine the concentrations in the test mixture. The data for each of the C<sub>4</sub>–C<sub>6</sub> hydrocarbons and carbon dioxide shows that a single standard can be used to determine an unknown at least within the concentration ranges of the standards studied (see Table 1). Choosing one of these

hydrocarbons to illustrate, data for *n*-butane fitted to a linear regression is shown in Table 4. The RF values are all within 1.2% over a factor 15 concentration range and show neither a downward or upward trend but are random, which suggests linearity. The difference (%) residuals support this as they are randomly plus or minus. Table 5 shows the concentration determination of *n*-butane in the test mixture versus each individual primary standard. In each case, the predicted concentration is well within the expanded uncertainty of the concentration, 0.2022% mol/mol ± 0.0018% mol/mol (±0.9% relative) determined from linear regression. Thus, in this case, a single standard can be used to determine the *n*-butane concentration.

Table 5  
The *n*-butane concentration determined vs. each primary gravimetric standard from 0.5 ml sample loop data

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration (% mol/mol) <sup>b</sup>	Concentration in test mixture vs. primary standard (% mol/mol) <sup>b</sup>	Difference (%) from regression value (0.2022% mol/mol)
CAL7493	0.4808 ± 0.0021	0.0976 ± 0.0001	0.2030 ± 0.0018	0.4
X16115	0.5038 ± 0.0022	0.1024 ± 0.0001	0.2033 ± 0.0018	0.5
X16156	0.9501 ± 0.0029	0.1925 ± 0.0002	0.2026 ± 0.0013	0.2
X16140	1.0002 ± 0.0041	0.2021 ± 0.0002	0.2021 ± 0.0017	−0.1
X16136	1.3940 ± 0.0046	0.2819 ± 0.0003	0.2022 ± 0.0014	0.0
X16106	3.973 ± 0.024	0.7973 ± 0.0008	0.2007 ± 0.0024	−0.7
CAL014774	5.002 ± 0.012	1.0101 ± 0.0010	0.2020 ± 0.0010	−0.1
X16157	7.066 ± 0.032	1.4226 ± 0.0014	0.2013 ± 0.0018	−0.4

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as standard deviation.

<sup>b</sup> The true concentration of *n*-butane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

Table 6  
Methane data obtained using 0.1 ml sample loop plotted to linear regression

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration <sup>b</sup>	Response factor (RF)	Predicted concentration <sup>b</sup>	Difference <sup>c</sup> (%)
X16157	0.7897 ± 0.0005	64.66 ± 0.06	0.01221	64.60 ± 0.10	−0.09
X16140	0.8500 ± 0.0005	69.53 ± 0.06	0.01222	69.53 ± 0.11	0.00
X16136	0.9302 ± 0.0016	76.06 ± 0.08	0.01223	76.10 ± 0.27	0.05
CAL7493	0.9869 ± 0.0010	80.69 ± 0.08	0.01223	80.73 ± 0.18	0.05
X302429	1.0002 ± 0.0028	81.82 ± 0.08	0.01222	81.82 ± 0.47	0.00
X16106	1.0346 ± 0.0008	84.60 ± 0.08	0.01223	84.64 ± 0.16	0.05
X16115	1.1090 ± 0.0011	90.67 ± 0.09	0.01223	90.72 ± 0.22	0.06
X16156	1.1533 ± 0.0009	94.46 ± 0.09	0.01221	94.35 ± 0.20	−0.12
Test mixture	1.0000	81.80 ± 0.20			

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as  $1\sigma$ .

<sup>b</sup> The true concentration of methane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

<sup>c</sup> The difference (%) is calculated from: [(predicted concentration − gravimetric concentration)/gravimetric concentration] × 100.

Since the methane set of data clearly shows that biased results may be obtained using just one standard, a second experiment was devised. The same column and detector were used but the 0.5 ml sample loop was replaced with a 0.1 ml. The data in Table 6 illustrates that the range of difference in the RF values for the primary standards is less than 0.2%. There is definitely no trend in the RFs, as they appear to be random with concentration indicating a linear regression is appropriate. The concentration predicted for the test mixture from this linear regression is only 0.15% different from the manufacture value. Table 7 shows the calculated concentrations for the test mixture versus each of the eight primary standards. The relative percent dif-

ference between the predicted test mixture value, determined from linear regression in Table 6, versus the values determined from each individual primary standard is no greater than 0.11%. These differences are all within the uncertainty limits of the concentrations. Once again, the data for nitrogen, ethane and propane show the same type of trend.

This analytical procedure, use of a 0.1 ml sample loop, would allow an analyst to use one reference standard that may be greater than 1% from the target concentration of the methane. The drawback is that the C<sub>4</sub>–C<sub>6</sub> compounds have such a low response to the detector at these concentration levels that the results are not as reproducible. In the analysis sequence,

Table 7  
Methane concentration determined vs. each primary gravimetric standard

Primary standard	Response ratio <sup>a</sup>	Gravimetric concentration (% mol/mol) <sup>b</sup>	Concentration in test mixture vs. primary standard (% mol/mol) <sup>b</sup>	Difference (%) from Regression Value (81.80% mol/mol)
X16157	0.7897 ± 0.0005	64.66 ± 0.06	81.88 ± 0.13	0.10
X16140	0.8500 ± 0.0005	69.53 ± 0.06	81.81 ± 0.13	0.01
X16136	0.9302 ± 0.0016	76.06 ± 0.08	81.76 ± 0.29	−0.05
CAL7493	0.9869 ± 0.0010	80.69 ± 0.08	81.76 ± 0.18	−0.05
X302429	1.0002 ± 0.0028	81.82 ± 0.08	81.81 ± 0.47	0.01
X16106	1.0346 ± 0.0008	84.60 ± 0.08	81.77 ± 0.16	−0.04
X16115	1.1090 ± 0.0011	90.67 ± 0.09	81.76 ± 0.18	−0.05
X16156	1.1533 ± 0.0009	94.46 ± 0.09	81.90 ± 0.16	0.11

<sup>a</sup> The uncertainty in the response ratio is calculated from the standard deviations of replicate analysis for the test mixture and the standards and reported as  $1\sigma$ .

<sup>b</sup> The true concentration of methane is expected, with 95% confidence, to be in the interval defined by the expanded uncertainty.

replicate injections are made from a sample before moving to the next. The average of the three resulting GC area responses and the standard deviation are calculated. Under these analytical conditions, the standard deviations of replicate analyses for the other hydrocarbons can be as large as 3%. These results are not reproducible to acceptable levels resulting in increase uncertainties in the concentrations for an unknown to the 5–10% level, well above the 1% or less range typically considered acceptable.

#### 4. Conclusions

There are many different instruments and configurations for analyzing natural gas, and this study only dealt with one selected method. However, results of this study, using the instrumentation as described, show that it is very important to understand the analytical system and its limitations when performing natural gas measurements. It is evident that sample size injected onto the analytical column has a significant role in the methane, nitrogen, ethane and propane measurements. Too much sample possibly overloads the column or detector, thus resulting in a lower response than expected at the higher concentrations (non-linear response). This would result in lower RF values and bias the concentration determined for a sample. It is desirable to choose analytical conditions that result in total analysis of a sample with just one method. The 0.1 ml sample loop does not result in reproducible results for many of the compounds of interest but results in more linear capabilities for methane, nitrogen, ethane and propane. The 0.5 ml sample loop introduces a large enough sample on the analytical column to give reproducible results for all the compounds of interest, but appears to overload the column for methane, nitrogen, ethane and propane. Using a suite of standards to determine the methane using second-order regression techniques can circumvent this problem. However, the nitrogen and methane elute very close together and this could also have an effect on the results when using a larger sample injection.

While the method described in the paper utilized the TCD, flame-ionization detection has a greater dynamic range. This would result in an increase in sensitivity for the minor components, thus possibly making it a

useful replacement to the TCD. However, much like increasing or decreasing the sample size, the FID versus the TCD will have the same issues. To achieve the increased sensitivity will also require a larger sample size which will result in saturation of the FID by the methane. This will also cause baseline interferences between some of the early eluting, high concentration compounds such as nitrogen, methane and ethane. Even the TCD at high sensitivity will be saturated if the sample size is large. Therefore, there is a balance between sample size, detector, and the amount of data that the analysts are willing to accept.

Complex gas matrixes, such as natural gas, make this a more difficult task due to the large differences in concentrations: as much as 1000-fold. The choice of the analytical column for this study permitted for all the compounds in the natural gas mixture to be detected and measured. Many analysts, as well as the International Organization for Standardization documents, utilize packed columns [11]. This does not rule out the use of capillary columns as there are also ISO documents for determination of the components of natural gas [12]. To accurately determine the behavior of an analytical system, a suite of standards becomes necessary. The system must be calibrated over a wide range of concentrations to understand its performance. Only then should analysts have confidence in using one standard for subsequent analyses. Even then the system should be periodically checked using a suite of standards to assure consistent instrument behavior. The analyst who has only one standard available runs the risk of obtaining biased results, which may significantly effect the ultimate product or price. Ultimately, one standard alone is not sufficient for natural gas measurements since the instrument should be calibrated and characterized over a wide concentration range, requiring more than one reference standard.

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