

REAL-TIME OPTICAL BTU MEASUREMENT OF NATURAL GAS AT LINE PRESSURE

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ABSTRACT

A method and device have been developed which accurately measure the BTU content of hydrocarbons at pipeline conditions. The cost of this device will allow some users who currently collect samples to have the advantages of on-line BTU measurement. The device measures, reports, and logs the BTU value per unit volume several times per minute. As the cell is nearly isobaric with the pipeline, the energy flow through the pipeline can be computed directly as the product of the BTU value per unit volume times volumetric flow rate.

BTU and composition are measured via optical absorption spectroscopy in the vicinity of 900 nm using a spectrograph and a silicon array detector. In contrast to longer infrared wavelengths, the natural gas absorption spectrum in this spectral region is a linear combination of the spectra of the component species. The observed spectrum can therefore be accurately fit to yield the concentration, in molecules per unit volume, of all C1 to C6 hydrocarbon components and water. The energy content of the components is then summed to yield the BTU per unit volume. Additional information such as the compressibility, density, and specific gravity can also be obtained from the measured gas compositions.

INTRODUCTION

The science of measurement of Natural Gas has gone through a technological revolution over the last 20 years. We have moved from the chart recorder with its limitations and built in delay of information to the widespread use of Electronic Flow Computers used to calculate volume and flow rate. Many of these are coupled with communication devices that supply updates of volumes on a "Real-Time" basis.

Concurrent with this development, the science of determining the BTU content of natural gas has gone through a series of changes from the Gas Calorimeter to the Field Gas Chromatograph. The Field Gas Chromatograph has become widely accepted and is used at many measurement locations. The Chromatograph does fulfill the function of providing accurate analysis of natural gas and does offer the capability of providing real-time information on gas analysis and, through calculation, BTU content.

There has long been a concern among many in the industry about the possibility of errors that might be introduced to the Gas Analysis by measuring the volume of the Natural Gas at line

pressures and conditions, and then conducting the Gas Analysis at one atmosphere of pressure. The concern has long been that when the pressure of the gas is reduced that the “Heavy Ends” may fall out. This is usually referred to as “Pressure Reduction Effect” and can cause a degradation of heating value or BTU’s. There has been very little work done within the industry to determine this level of error or to correct the situation due mainly to the fact that no apparent alternative existed.

Due to the current price of Gas Chromatographs however, the industry has been able to install them only on measurement locations with sufficient volume to justify the cost. In most companies this translates to stations with a volume of 25 to 30 MMSCFD or more. On stations with smaller volumes, composite samples are still being taken. With the delay involved in having these samples analyzed in a lab, the Gas Analysis and BTU information can easily take 2 weeks or more before it can be applied to the volumetric information obtained on a “Real-Time” basis through an Electronic Flow Computer.

This of course is not a desirable situation. FERC order # 636 is pushing the industry to provide “Daily” information on both gas volume and gas quality. Add to this the fact that more and more Gas Contracts are being written on a BTU basis and it becomes quite apparent that something new is needed in the Natural Gas Industry to enable “Real-Time” gas quality information to be gathered at stations with smaller and smaller volumes.

All of these conditions prompted Spectral Sciences, Inc., a “High-Tech” Research company involved in using light to detect and define various gases, and PERRY Equipment Corporation, which provides engineered products and Systems for filtration and measurement for the Oil and Gas industry, to form a cooperative development project to develop and market an OPTICAL BTU MONITOR.

The design goals for the Optical BTU Monitor include:

- 1) real-time continuous measurement at line conditions,
- 2) minimal field calibration,
- 3) a selling price below that of current gas quality instrumentation, and
- 4) the following data products:
 - a. BTU/volume at line conditions,
 - b. BTU/volume under standard conditions,
 - c. compressibility,
 - d. C1-C6+ mole fractions, and
 - e. water content.

TECHNICAL BACKGROUND

The design goals can all be met using near-visible absorption spectrometry in the 900 nm spectral region to quantify the energy content of high-pressure gas mixtures. The feasibility of this approach was first proven in a Department of Energy-funded research program conducted by Spectral Sciences. SSI developed, demonstrated, and patented⁽¹⁾ techniques for the accurate determination of BTU and component compositions over a thousand-psi pressure range.

Our Optical BTU Monitor is conceptually similar to other spectroscopic BTU sensors that use longer wavelength radiation in the Near IR (1000-2000 nm) and Mid IR (3000-5000 nm) spectral regions⁽²⁻⁵⁾. The significant differences, arising from the nature of the absorption spectrum in the near-visible (900 nm) region, are enumerated below.

First, at shorter wavelengths there is a strong correlation between the measured absorption and the BTU content. This phenomenon can be understood within the context of local mode theory, whose validity was established in a series of measurements of the alkane hydrocarbon absorption spectra in the 1980s⁽⁶⁻⁷⁾. According to local mode theory, as the wavelength decreases, the absorption features become more and more characteristic of the local CH bonds (differentiated as CH₄, CH₃, CH₂, and CH functional groups) rather than the molecule as a whole. As the BTU content of the molecule is also determined by the number and nature of the chemical bonds, the strength of these functional group absorption features are a direct measure of the BTU value. The detailed shape of the spectrum provides sufficient additional information to perform a detailed component analysis, yielding C1-C6+ component concentrations with a mole fraction accuracy of better than 1%. Because all of the molecular components have nearly the same absorption strength per BTU content, the measured total BTU content is more accurate than the individual component concentrations and is typically better than 0.1%, or 1 BTU/SCF.

A second advantage of working near 0.9 microns is that, in contrast to longer wavelengths, the hydrocarbon absorptions increase linearly with molecular density (at 1-5 nm spectral resolution)^(3,8). This allows for a simple and accurate calibration based on the decomposition of the sample spectrum into a linear combination of component spectra representing the absorptions and concentrations of the component molecules. This kind of first-principles calibration is generally applicable over the entire range of natural gas compositions and pipeline pressures. Therefore no detailed on-site calibration of the sensor is required.

Third, the near-visible absorption spectrum falls within the response range of standard silicon CCD detectors used in digital cameras. Our device takes advantage of low-cost commercial digital camera technology to record the absorption spectrum with a fidelity that is difficult, if not impossible, to achieve with more costly detectors used at longer wavelengths.

Finally, absorptions in the 900 nm spectral region are much weaker than those observed at longer wavelengths. The maximum absorption detection sensitivity is achieved with a cell length of about 2 feet at pressures of about 500 psi, making this an ideal spectral region for measuring at pipeline conditions.

Continuous monitoring at line conditions also provides a number of advantages. The primary advantage is the reduction in sampling error compared with methods, such as gas chromatography, which require expanding the gas to one atmosphere prior to analysis. The second advantage is that the primary data product is the energy content per unit volume at line pressure. When used in conjunction with a volumetric flow meter, this yields a more accurate value of energy flow rate than can be obtained by independent measurements of the energy content and compressibility at low pressure. Finally, the Optical BTU Monitor makes a continuous measurement of the gas flowing through the sample cell with a response time of less

than a minute, providing a route to the calculation of energy content and energy flow rate on a continuous basis.

METHOD OF OPERATION

Figure 1 shows the overall layout of the Optical BTU Monitor and a typical installation adjacent to an orifice flow meter, Measuremaster fitting, and flow computer. A small sampling line is used to divert a fraction of the pipeline gas through the sample cell and back into the pipeline. The sampling is nearly isokinetic and isothermal; that is, the sample cell temperature and pressure closely match those of the pipeline gas. The pressure drop in the sampling line is of order 0.1 psi, and the residence time in the cell is of order 10 seconds. The pressure, temperature, and transmission spectrum of the gas in the cell are measured with appropriate sensors and the signals are routed to a control/monitoring system for analysis. In a typical installation, the resulting energy values and compressibility would be transmitted to the flow computer, which in conjunction with its gas volumetric information, would calculate the “Real-Time” energy flow rate.

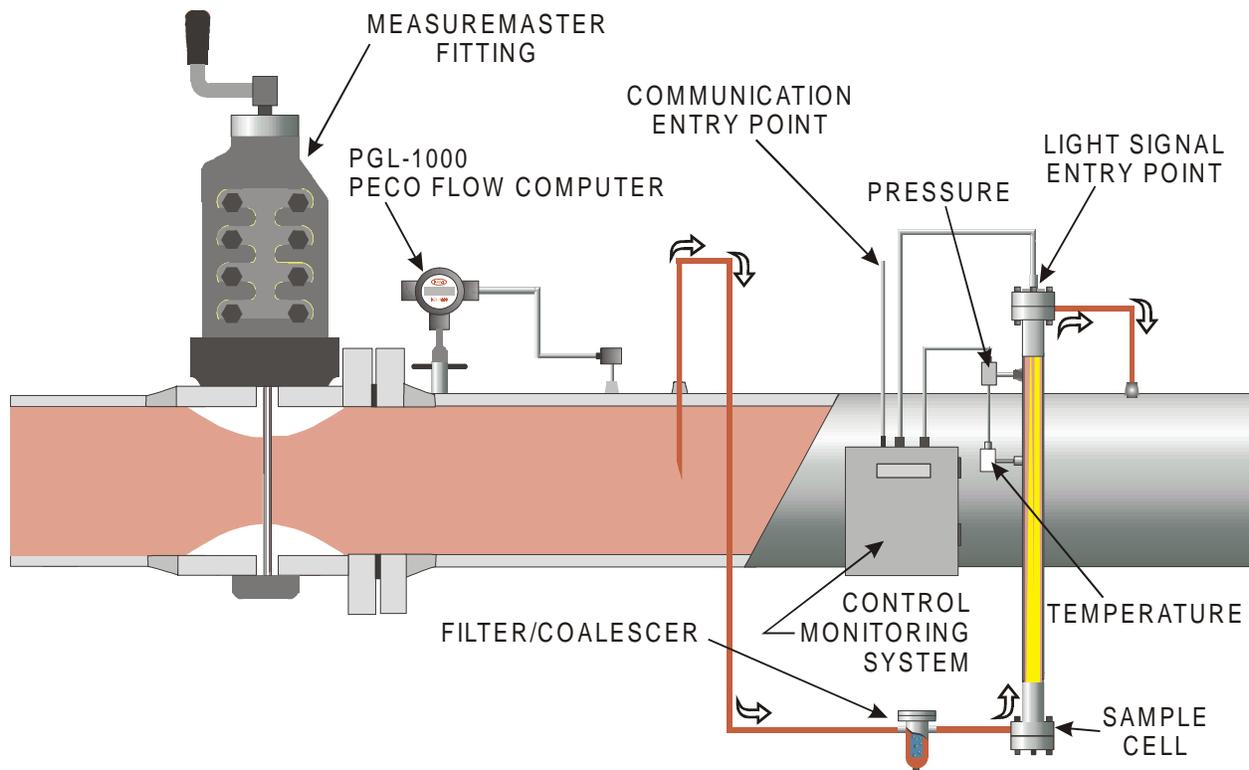


Figure 1. Typical installation of Optical BTU Monitor Adjacent to an Orifice Flow Meter.

Figure 2 shows the functional components of the monitoring system. Light generated by an incandescent lamp is routed to the sample cell and back using optical fibers. The spectrum of the returned light is recorded using a concave holographic grating spectrograph and a silicon CCD detector. An auxiliary CO₂ detector built into the spectrograph monitors the CO₂ concentration in the sample cell. The internal signal processing unit records the CCD images, temperature, pressure, and CO₂ data; averages multiple CCD images; converts the CCD images

into an absorption spectrum; decomposes the absorption spectrum into component spectra; and calculates component concentration, BTU, and compressibility from the component fit coefficients and measured temperature and pressure. This measurement cycle is repeated with a period of 20 seconds. The 20-second data is output to the optional data port and logged at 2-minute intervals. Hourly and daily averages are also computed and stored internally.

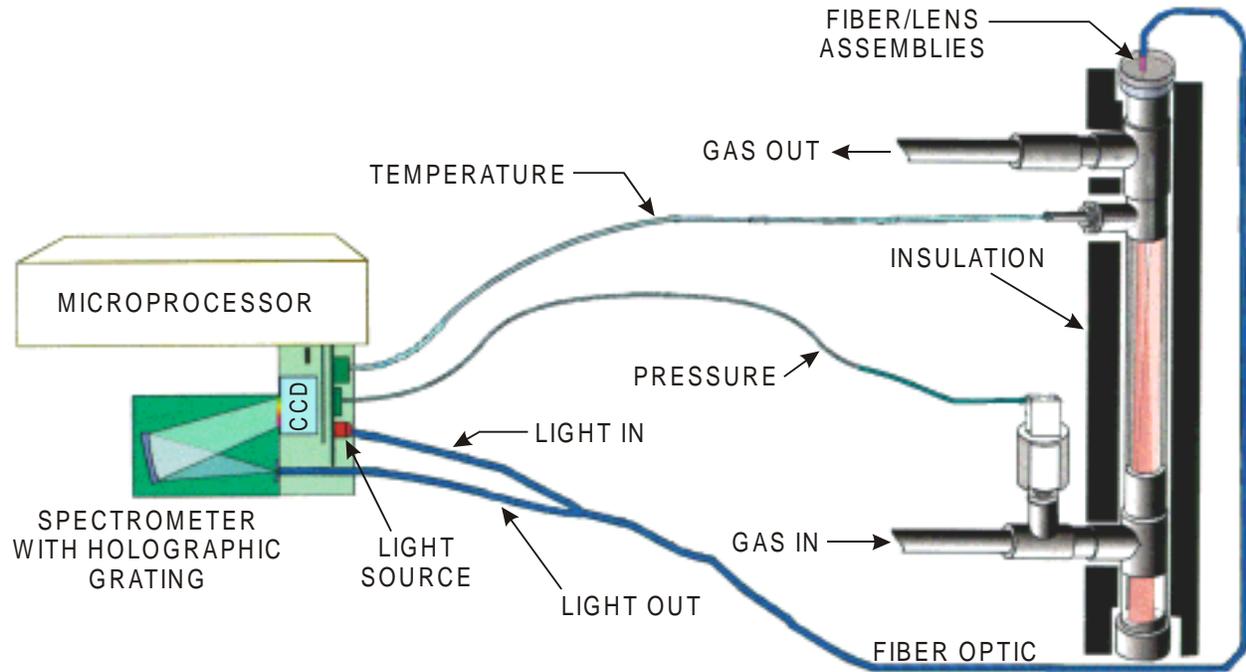


Figure 2. Cutaway View Showing Major Elements of the Control/Monitoring System and Sample Cell.

Measurements of a Known Gas Mixture

The following figures demonstrate the operation of the Optical BTU monitor using data sets collected for a pre-analyzed standard gas mixture over a pressure range of 125-980 psi in a 4-foot sample cell. The stated gas composition was: 88.5% methane, 5% ethane, 1% propane, 0.5% n-butane, 0.5% I-butane, 2% CO₂, and 2.5% N₂. Data sets were collected for 20 hour periods at a variety of pressures and analyzed to determine component densities, ρ_i (in units of standard atmospheres of ideal gas), energy content per unit volume, BTU/Cu. Ft., and compressibility, Z . These primary results were then used to compute the energy content at standard conditions, BTU/SCF (BTU per Standard Cubic Feet), and component mole fractions. The methods used to produce these data products are outlined below using typical data.

Figure 3 shows a typical hydrocarbon absorption spectrum, $f(\lambda)$, and several of the fit component spectra. Data recorded for 20 seconds at a pressure of 375 psi are presented in absorption units, $f(\lambda) = -\ln(T(\lambda))$, where $T(\lambda)$ is the fractional transmission of the gas. The spectral data are fit using a function, $g(\lambda)$, constructed from 16 component basis spectra, $B_i(\lambda)$,

to determine the component densities, ρ_i , which minimize the differences between $f(\lambda)$ and $g(\lambda)$:

$$g(\lambda) = \sum_{i=1}^N \rho_i B_i(\lambda)$$

The component spectral basis set represents the absorption spectra of the 13 C1-C6 hydrocarbon isotopes, water, and instrument baseline terms. The fit densities of all of the molecular components are tabulated in Table 1, and compared to our best estimate of the prepared value based on the stated mole fractions, X_i , and measured temperature, T, and pressure, P, using the non-ideal gas law of partial pressures

$$\rho_i = X_i \frac{P}{Z RT}$$

and the compressibility Z, calculated by the AGA8z method. The fit molecular densities for the five C6 isotopes have been grouped together into a common output C6⁺.

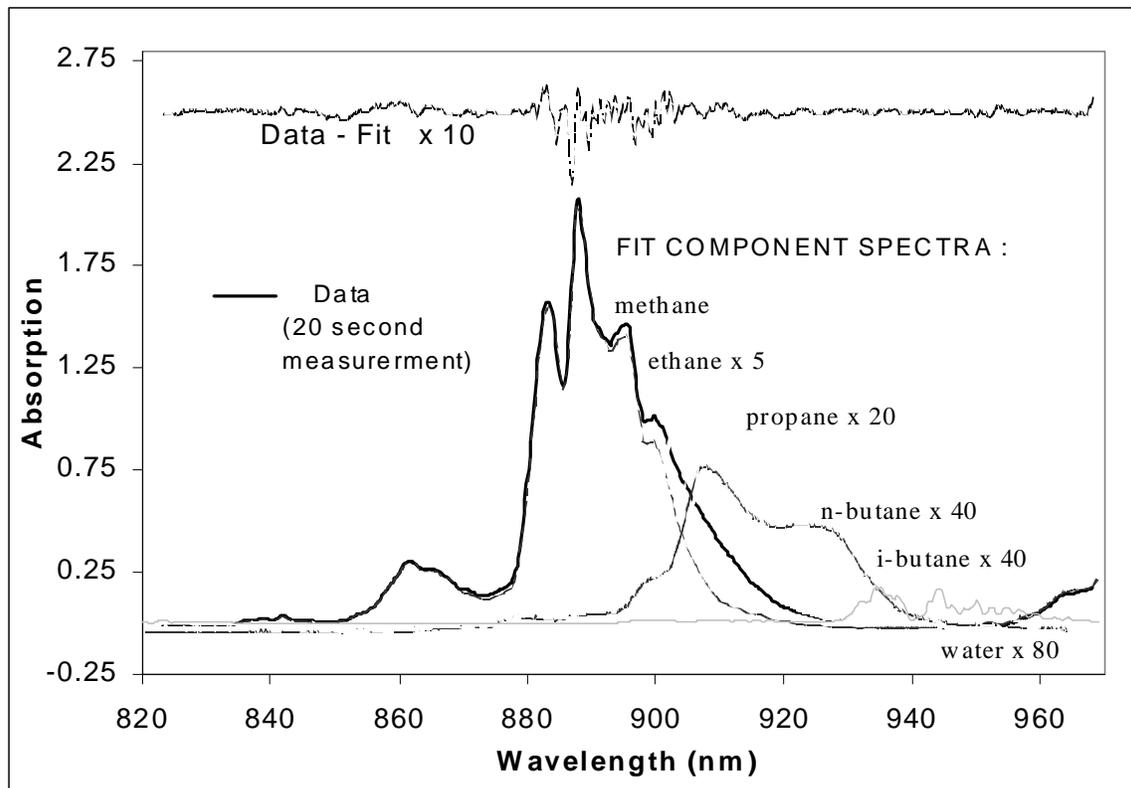


Figure 3. Measured Absorption Data and the Major Components used in the Fit for a Typical 20-second Measurement.

Figure 3 displays the resulting component spectra, $\rho_i \times B_i(\lambda)$, for the six significant molecular components found in the fit. The component spectra have been multiplied by scaling factors of 5, 20, 40, or 80 for display purposes. The top trace displays the difference between the data and the fit spectrum magnified by a factor of 10. The majority of the errors in the fit occur in the vicinity of the main methane peak near 900 nm where the error in the fit spectrum is of order 1% of the measured absorbency or 0.1% of the transmitted intensity. This error in the fit absorption spectrum has little or no effect on the fit densities, as the methane peak is isolated from the other hydrocarbon absorption peaks. Away from the peak absorption, the error is representative of instrument error and is characterized by an RMS error of $\Delta I/I_0=0.06\%$.

Table 1. Fit and Prepared Values for ρ_i in Units of Standard Cubic Feet of Ideal Gas.

	$\rho_{methane}$	ρ_{ethane}	$\rho_{propane}$	$\rho_{n-butane}$	$\rho_{1-butane}$	$\rho_{n-pentane}$	$\rho_{1-pentane}$	$\rho_{neopentane}$	ρ_{C6+}	$\rho_{hydrocarbon}$	ρ_{water}
Fit	22.85	1.30	0.28	0.11	0.11	0.00	0.01	0.00	0.00	24.65	0.0044
Prepared	22.80	1.29	0.25	0.13	0.13	0.	0	0	0	24.60	0
$\Delta\rho_i / \rho_{hydrocarbon}$	0.20%	0.05%	0.11%	-0.09%	-0.08%	0	0.04%	0	0	0.22%	0.00017%

The component spectra shown in Figure 3 display clear qualitative differences. The major methane absorption features are well separated and clearly distinct from the C2-C6 component spectra. The latter display a series of common features occurring at successively longer wavelengths, that can be associated with the CH₃, CH₂, and CH functional groups, respectively. At even longer wavelengths, a highly structured water absorption is observed. A closer examination of the component spectra reveal subtle differences in the shape and position of the spectral features, including a large number of weaker features at shorter wavelengths, that distinguish the various component spectra from each other. Therefore the fit tends to give compositional results that are very similar to the known composition of the gas. For example in this data, all component densities were fit with an absolute error, as defined by of the fraction of the total hydrocarbon density, $\Delta\rho_i / \rho_{hydrocarbon}$, of less than 0.2%.

The energy content per unit volume, BTU/Cu. Ft., is calculated by multiplying the fit component densities ρ_i by the standard BTU values of the components, E_i , (in units of BTU/standard cubic feet of ideal gas):

$$BTU / Cu.Ft. = \sum_i \rho_i E_i$$

For the data presented in Figure 3 and Table 1, the fit and prepared BTU/Cu. Ft. differ by 0.07%. These data are typical in that the BTU/Cu. Ft. value is more accurate than the fit component densities due to cancellation of errors in the individual component densities. Figure 4 shows a record of the fit BTU/Cu. Ft. value recorded at 2-minute intervals over a period of six hours. The Optical BTU Monitor data show a linear decline with time due to a slow leak in the cell. The data fit a straight line with an RMS error of 0.04%. Figure 4 also plots the BTU/Cu. Ft. computed for the standard gas composition and measured temperature, T, pressure, P, and known compressibility of the mixture, Z. The two curves follow a similar trend. The larger variation observed in the computed value reflects the errors in the pressure and temperature measurements.

Figure 5 plots the fit component densities over the same time period. A logarithmic scale is used to display all of the component densities on a common scale. The five C1-C4 components known to be in the mixture appear with the component densities reported in Table 1. The typical measurement-to-measurement fluctuation in component densities is of the order of 0.01 standard atmospheres, or less than 0.1% of the total density. Isopentane, which is not in the sample cell, is reported with a density less than 0.01 standard atmospheres. The other C5 and C6 component densities are identically zero for most measurements.

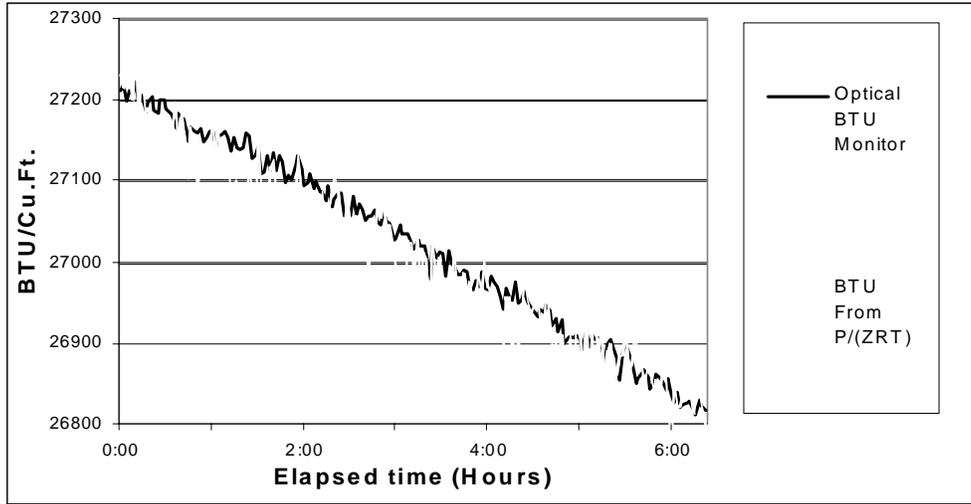


Figure 4. BTU/Cu. Ft. as a Function of Time as determined by the Optical BTU Measurement and the Pressure and Temperature Measurement. Each Data Point Corresponds to a Single 20-Second Measurement as Shown in Figure 3.

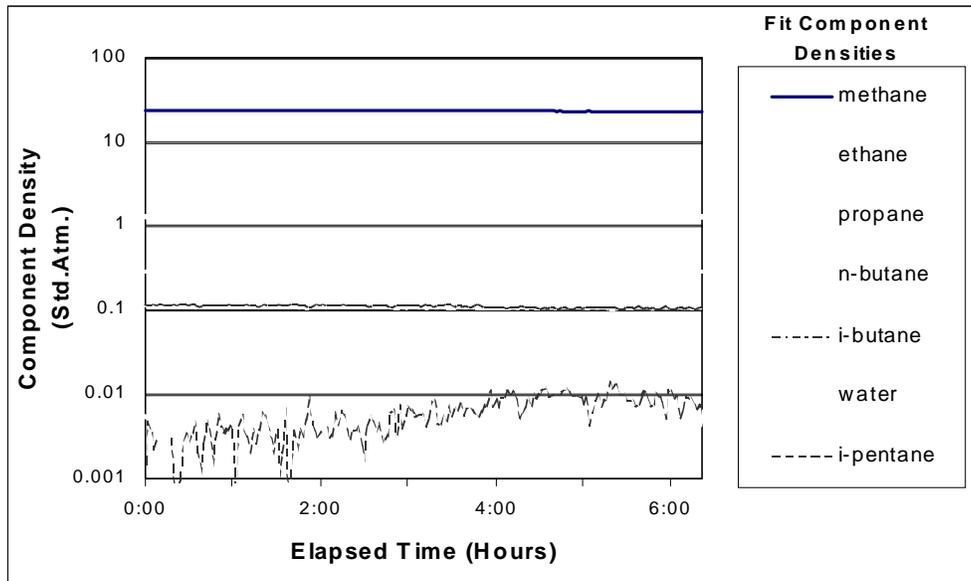


Figure 5. Fit Component Densities as A Function of Time. Components with Fit densities less than 0.0002 Standard Atmospheres (0.001% Mole Fraction) are not shown.

The water density measurement is more sensitive than the hydrocarbon density measurement as the water absorption is substantially stronger. The measured water values plotted in Figure 5 correspond to a mole fraction of $0.017 \pm 0.02\%$ or 8 ± 1 pounds per MMSCF and a dew point of 23°F . This value is consistent with water out-gassing in the sample cell and gas cylinder.

Calculation of Compressibility and Projection to Standard Conditions

In order to convert the measured hydrocarbon densities to mole fractions, the total density, ρ_{total} , must be determined by solving the non-ideal gas equation of state.

$$\rho_{total} = \frac{P}{ZRT}$$

The total density is the sum of the measured densities of hydrocarbons and water, plus the density of inert compounds such as N_2 and CO_2 which do not contribute to either the absorption spectrum or the BTU value. The compressibility and the total density can be determined simultaneously by detailed balance using iterative techniques. For a natural gas mixture, the compressibility is nearly independent of composition and varies from 1 to 0.85 with increasing pressure. The variation with gas composition is determined primarily by the molecular interactions of the hydrocarbon gases and is nearly independent of the identity of the minor inert chemical constituents. Therefore, an iterative solution of the equation of state quickly converges to yield the compressibility and inert gas density. Following industry practice, compressibility is calculated by method AGA8z with the simplifying assumptions that all measured C6+ density is attributed to n-hexane and measured neo-pentane is attributed to n-pentane and i-pentane. The N_2 and CO_2 mole fractions are estimated based on the previous measured values, the compressibility is calculated, and any differences between the density computed by the equation of state and the input density is attributed to N_2 and CO_2 .

Once the calculation has converged, the total density, ρ_{total} is calculated from the equation of state, and the mole fractions are determined from

$$X_i = \frac{\rho_i}{\rho_{total}}$$

The compressibility is calculated by method AGA8z using the component mole fractions, and the BTU value is projected to standard conditions by:

$$BTU / SCF = \sum_i X_i \frac{E_i}{Z_o} = BTU / Cu.Ft. \left(\frac{TZ}{P} \right) \left(\frac{P_o}{T_o} \right)$$

to yield Energy content in units of standard cubic feet of ideal gas.

For gas mixtures at pressures less than 800 PSI and inert gas mole fractions less than 5%, the compressibility can be computed with an accuracy better than 0.05% with no detailed knowledge of the CO₂ concentration. In the Optical BTU Monitor, we use an auxiliary CO₂ sensor to determine the CO₂ mole fraction independently, thereby yielding a slightly more accurate compressibility calculation.

Figure 6 plots the computed compressibility for the data set displayed in Figures 4-5. Each data point represents a 20-second measurement. The straight line is the best fit to the measured temperature and pressure trends using the compressibility calculated for the standard gas mixture. The scatter in the measured compressibility arises primarily from the scatter in the temperature data. The compressibility error is of the order of 0.02% and reflects the 0.2% error in the measured heavy hydrocarbon mole fractions.

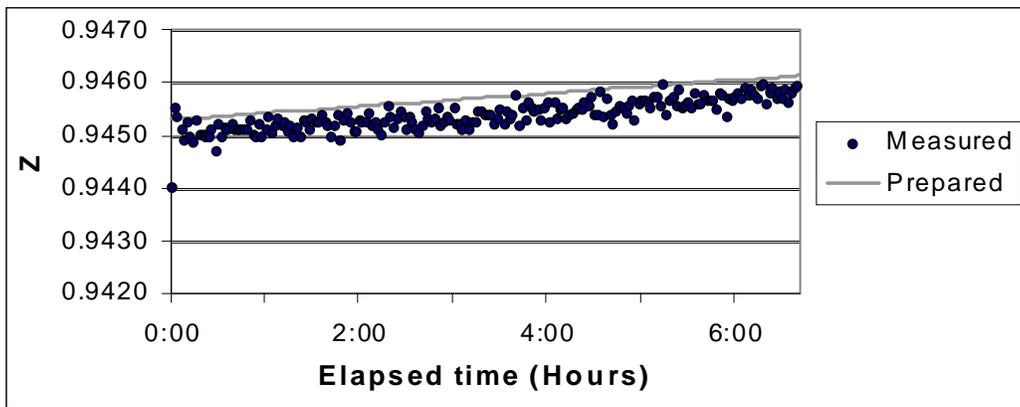


Figure 6. Measured Compressibility for the Data of Figures 5 and 6.

Figure 7 plots the measured energy content of the gas in units of BTU/SCF. The average value of 1040.6 BTU/SCF is 0.02% or 0.2 BTU/SCF greater than the stated value of the mixture, 1040.4 BTU/SCF. The RMS error in the 20-second data points of is 0.5% or 0.5 BTU/SCF. This is slightly greater than the error in the average BTU/Cu. Ft. value because of the additional error in the temperature and pressure measurement.

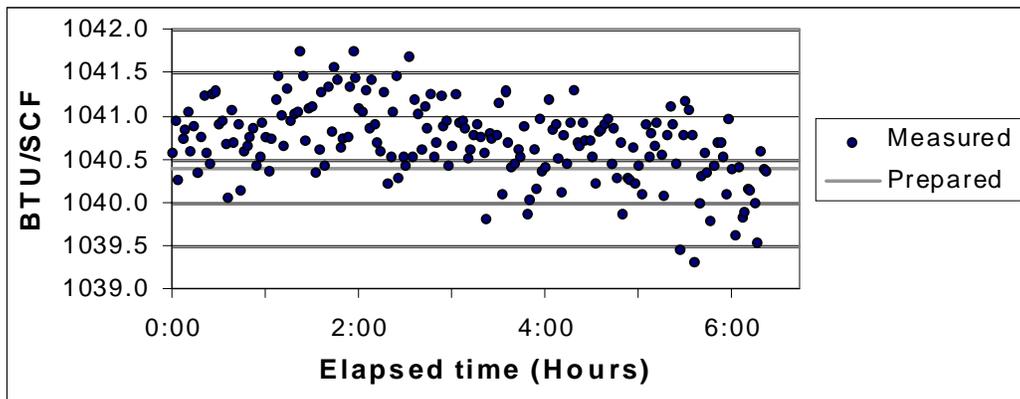


Figure 7. Data of Figure 5 Expressed as BTU/SCF.

Summary Data

Figures 8-9 summarize the BTU measurement results over the entire range of pressures. Figure 8 plots the average BTU/SCF value measured for each pressure condition. The error bars represent the estimated error based on the uncertainty in the temperature and pressure reading. Data averaged over 16-24 hours are distinguished from those averaged over 1-6 hours. The average values are all within 1 BTU/SCF of the stated value of the mixture. Figure 8 plots the RMS error of the reported BTU/Cu. Ft., and BTU/SCF for each of the data sets. The RMS error for the BTU/Cu. Ft. is less than 0.05% at all pressures. The RMS error in the BTU/SCF is less than 0.6% or 0.6 Btu/SCF for all pressures below 850 PSI.

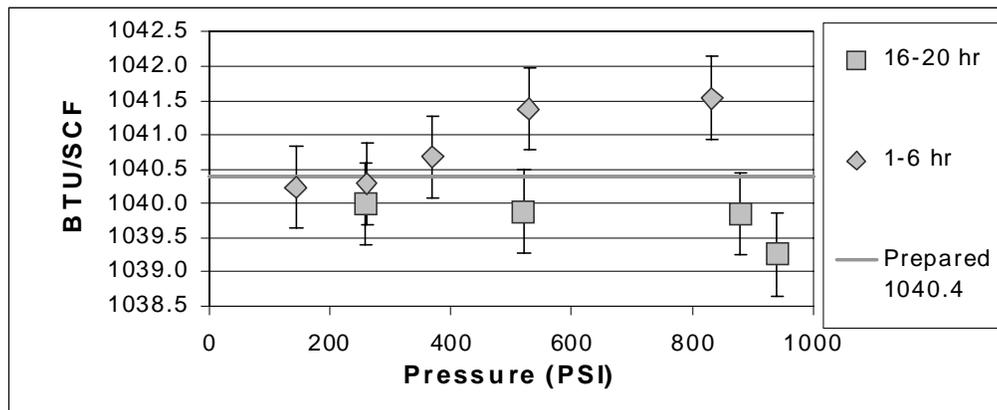


Figure 8. Average BTU/SCF Measured over a Multiple-Hour Period at a Variety of Pressures.

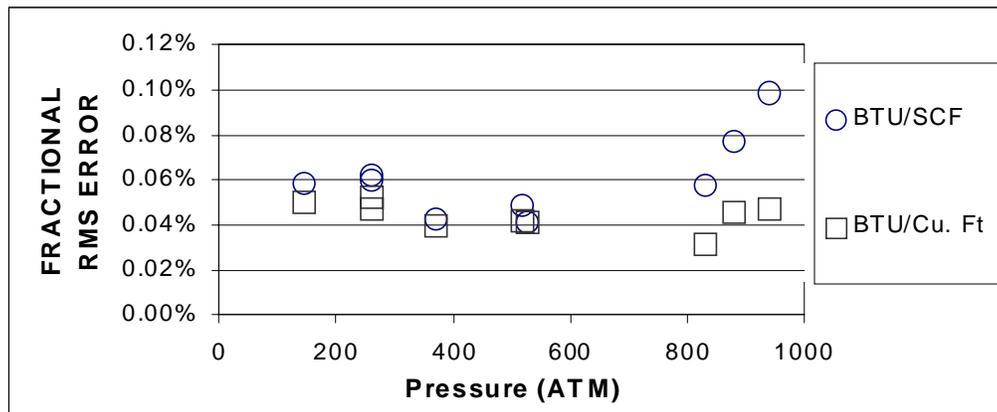


Figure 9. Fractional RMS Error in the Measured BTU/ CU. Ft. and BTU/SCF for the Data Sets shown in Figure 8.

At higher pressures, the RMS errors in BTU/SCF increase, approaching 1 BTU/SCF at 1,000 PSI. This trend reflects the sensitivity of the high-pressure compressibility to small errors in the mole fractions of heavy hydrocarbons. For example, at 1000 PSI, a 0.1% error in the isopentane mole fraction will result in a 0.13% error in Z. The error in Z does not affect the measurement of the energy content at pipeline pressure (BTU/Cu. Ft.), but only the value projected to standard conditions (BTU/SCF). If the BTU value is being measured to determine

the energy flow rate in the pipe, the projection of energy content to standard conditions is unnecessary.

It is important to note that errors in the calculated compressibility depend only on the component mole fraction errors and reflect all of the errors in the composition measurement including sampling errors and measurement errors. Compressibility calculated from gas-chromatographic analysis at room pressure is routinely used in flow rate calculations. The resulting high-pressure compressibility suffers from systematic errors due to the "Pressure Reduction Effect". It is likely that composition measurements made at pipeline pressures will be more accurate than those made at atmospheric pressure and will provide more realistic compressibility values, thereby improving the accuracy and repeatability of the flow rate calculation.

MEASUREMENTS OF UNKNOWN PIPELINE GAS

At the time of writing (March 1999), preparations are underway to measure unknown pipeline gas under flowing conditions. The results of these measurements will be presented at the June meeting.

ADVANTAGES & APPLICATIONS

The lower initial cost of the SSI / PECO Optical BTU Monitor, in conjunction with lower long term maintenance costs, will most certainly aid the Natural Gas Industry in bringing "Real-Time" BTU and Gas analysis data to smaller volume stations. It may be possible to reduce the economical volume point where "Real-Time" BTU and Analysis data can be obtained to as low as 10 MMSCFD from 25 to 30 MMSCFD. This of course will exponentially increase the number of sites on which true "Real-Time" information can be obtained.

With more "Real-Time", accurate gas quality information coming from more and more measurement sites with smaller and smaller volumes, the Gas Industry should come closer to the goal of true "Equity of Exchange."

As pointed out above this device has the unique ability to analyze gas at line conditions. This ability will help eliminate the uncertainty currently associated with gas analysis, which is done at one atmosphere of pressure instead of at line conditions. Once again this should bring the Gas Industry closer to the goal of an accurate "Equity of Exchange."

Gas Chromatographs currently available do not have the ability to detect water and in fact can be damaged by the presence of water. Partially to eliminate water, extensive filtering and heating of the gas is done before it is allowed to enter the Gas Chromatograph. Typically, a Dew Point Monitor must be installed in conjunction with the Gas Chromatograph to determine water content.

The SSI / PECO Optical Gas Analyzer and BTU Monitor will not be damaged by water vapor that gets by the filtration system and enters the sample cylinder. In fact the device will measure and record the presence of any water and the dew point.

Most Gas Chromatographs make a single analysis every 3 to 4 minutes. A few devices make an analysis every 1-minute. The SSI / PECO Optical BTU Monitor makes an analysis every 30 seconds and this analysis is actually made up of images taken more often than once each second. This higher sampling rate gives the user much higher resolution. Higher resolution yields higher accuracy.

CONCLUSION

The Optical Gas Analyzer and BTU Monitor represents a quantum technological leap in the determination of BTU content and compositional make-up of natural gas. It's lower initial cost and lower maintenance cost will aid the Natural Gas Industry in obtaining "Real-Time" Gas analysis and BTU information at smaller volume stations.

Performing the Gas Analysis at "Line" conditions instead of reducing the pressure of the gas to one atmosphere, will help reduce the uncertainties that have been present in the technologies used up to the present time. The benefit to the industry will be that the industry can come closer to its goal of a true and accurate "Equity of Exchange" in Gas Measurement.

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