Carbon Content, Sampling, and Calculation

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Introduction

Carbon emission quantities can be calculated from either the volume/mass of fuel or feedstock fed to a process (as applicable) and carbon content of the process or fuel supply, or by directly measuring volume/mass emissions.

This Technical Report (TR) provides guidance on the sampling and calculation of carbon content of process or fuel supplies. The API companion technical report, API TR 2571, *Fuel Gas Measurement*, can be referenced for guidance on measuring the volume/mass of process fuel gas or feedstock, and the API *Compendium of Greenhouse Gas Emissions Estimation Methodologies for the Oil and Natural Gas Industry* can be reference for guidance on the calculation of emissions.

Carbon Content, Sampling, and Calculation

1 Scope

This Technical Report (TR) provides guidance and a methodology for determination of carbon content from hydrocarbon-based petroleum and petrochemical products, and the uncertainty of the average carbon content as calculated from multiple samples taken during a reporting period. This method is intended to make use of industry-accepted mixture property data and test methods with no new or modified test methods introduced in this document. The method is applicable to carbon-content-based reporting or trading for all gaseous and liquid hydrocarbons.

This TR provides references and supplemental information on applicable industry practices based on the published resources, existing industry standards, industry-accepted physical constants or properties of hydrocarbons for measurement, sampling, sampling frequency, and analysis of hydrocarbon samples.

2 Terms, Definitions, and Symbols

2.1 Terms and Definitions

For the purposes of this document, the following definitions apply.

2.1.1

accuracy

The ability of a measurement instrument to indicate values closely approximating the true value of the quantity measured.

2.1.2

bias

Any influence on a result that produces an incorrect approximation of the true value of the variable being measured. Bias is the result of a predictable systematic error.

2.1.3

calibration

The process or procedure of adjusting an instrument so that its indication or registration is in satisfactorily close agreement with a reference standard.

2.1.4

carbon content

The fraction of carbon in the fluid expressed as percent by weight.

2.1.5

compensation

The adjustment of the measured value to reference conditions (e.g. pressure compensation).

2.1.6

continuous emission monitoring system CEMS

The equipment required to sample, analyze, measure, and provide, by means of monitoring at regular intervals, a record of gas concentrations, pollutant emission rates, or gas volumetric flow rates, individually or in combination, from stationary sources.

2.1.7

flowing compressibility

The compressibility of the fluid at actual flowing temperature and pressure.

2.1.8

flowing density

The density of the fluid at actual flowing temperature and pressure.

2.1.9

fuel gas

Typically a mixture of light hydrocarbon and other molecules (e.g. H_2 , N_2) in a gaseous state that are consumed in fired heaters. Fuel gas is often a mixture of recovered gaseous molecules from plant operations and purchased natural gas.

2.1.10

higher heating value

HHV

The high or gross heat content of the fuel with the heat of vaporization included. The water is assumed to be in a liquid state.

2.1.11

influence parameter

Any factor that impacts the performance of the measuring device, hence the uncertainty and accuracy of the measurement. Examples are process temperature, pressure, fluid composition, upstream straight length, etc.

2.1.12

inspection

A visual assessment or mechanical activity (e.g. instrument lead line blow down or orifice plate cleanliness) that does not include comparison or adjustment to a reference standard.

2.1.13

meter condition factor

An estimate of additional uncertainty based on a technical judgment of the physical condition of the meter in lieu of the ability to inspect.

2.1.14

metering or measurement system

A combination of primary, secondary and/or tertiary measurement components necessary to determine the flow rate.

2.1.15

performance

The response of a measurement device to influence parameters such as operating conditions, installation effects, and fluid properties.

2.1.16

range of uncertainty

The range or interval within which the true value is expected to lie with a stated degree of confidence.

2.1.17

uncertainty

Describes the range of deviation between a measured value and the true value, expressed as a percentage. For example, a device with an accuracy of 2 % would have an uncertainty of ±2 %.

2.1.18

verification

The process or procedure of comparing an instrument to a reference standard to ensure its indication or registration is in satisfactorily close agreement, without making an adjustment.

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2.2 Symbols

For the purposes of this document, the following symbols apply.

AW _{Carbon}	atomic weight of carbon (e.g. 12.011)
CC	carbon content expressed as the weight fraction of carbon to the component
CC _{Average}	reporting period average carbon content
CC _{Mixture}	carbon content weight fraction of mixture
MW _{Component}	molecular weight of component (e.g. 44.0956 g/mole for propane)
MW _i	molecular weight of component <i>i</i>
п	the number of carbon atoms in the component (e.g. for propane, C_3H_8 , $n = 3$)
Xm _i	mole fraction of component <i>i</i>
Xw _i	mass fraction of component i
σ	standard deviation

3 Sample Collection and Handling

3.1 General

The primary purpose of sample collection and handling is to ensure that a representative sample of the product is taken and that the sample is handled in a manner that does not compromise composition of the sample.

3.2 Gas Fuel Sample Collection and Handling

API *MPMS* Ch. 14.1^[4] provides guidance on the sample collection and handling of natural gas and can also be applied to other gaseous fuel products.

3.3 Liquid Fuel Sample Collection and Handling

API *MPMS* Ch. 8.1 ^[1], API *MPMS* Ch. 8.2 ^[2], and API *MPMS* Ch. 8.3 ^[3] provide guidance on the sampling collection and handling of liquid petroleum and petroleum products.

3.4 Frequency of Sampling

Requirements for sampling frequency are related to their effect on the accuracy of reported carbon emissions and may impact the ability to achieve mandated or contractual targets. They are defined by contractual and/or regulatory requirements.

Section 6 provides a methodology that can be used to estimate the effect of sampling frequency on the uncertainty of facility-aggregated reporting period carbon emissions. These uncertainty estimates provide a basis for minimizing sampling frequency based on process variability.

4 Sample Analysis

4.1 Introduction

Reporting of carbon emissions from fuel combustion sources may require the determination of the fuel higher heating value (HHV) or carbon content from fuel samples.

4.2 Chromatographic Analysis of Fuel Samples

Chromatographic analysis of fuel samples can be used to calculate the fuel HHV and carbon content.

GPA, ASTM, and chromatograph manufacturer recommendations provide guidance for the analysis of the gas samples (see the Bibliography for a list of applicable standards).

GPA, ASTM, and AGA provide guidance for the calculation of HHV (see the Bibliography for a list of applicable standards).

Section 5.3 provides guidance for the calculation of carbon content from compositional analysis.

4.3 Test Methods for Determination of Carbon Content

In addition to chromatographic analysis of product samples, other technically acceptable standards for the determination of carbon content may be used, for example, ASTM D5291 ^[27] and ASTM D7662 ^[30].

5 Determination of Carbon Content and Calculation of Emissions

5.1 Introduction

Equations for the calculation of carbon content for a pure component and a product analysis presented here are based on the definitions found in Section 4.3 of the API *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry* ^[5], August 2009.

NOTE Values for atomic weight or molecular weight used in many references on carbon content determination are often reported to limited precision due to accuracy limitations of the methods being discussed. Numeric round-off, reflecting an appropriate number of significant digits, is considered acceptable only at the final stage of creating an emissions inventory to prevent compounding inaccuracy.

5.2 Carbon Content of a Pure Component

The carbon content of a pure component is defined as the ratio of the weight of carbon to the weight of the pure component. It can be calculated using the following equations:

$$CC = \frac{n \times AW_{Carbon}}{MW_{Component}}$$

where

- CC is the carbon content expressed as the weight fraction of carbon to the component;
- *n* is the number of carbon atoms in the component (e.g. for propane, C_3H_8 , *n* = 3);

AW_{Carbon} is the atomic weight of carbon (e.g. 12.011);

MW_{Component} is the molecular weight of the component (e.g. 44.0956 g/mole for propane).

5.3 Carbon Content Calculated from Product Analysis

5.3.1 General

The carbon content of a mixture is the weighted average of the individual component carbon contents and can be calculated from the compositional analysis of the mixture. Chromatographic analysis is generally reported by volume (mole fraction or mole percent) or mass (mass fraction or mass percent); therefore, calculations for both

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types of analysis are included below. Molecular weights of hydrocarbon components can be found in GPA 2145^[9], GPA TP-17^[18], and the *API Technical Data Book*, Chapter 1.

The following examples given in Table 1 and Table 2 are merely examples for illustration purposes only. They are not to be considered exclusive or exhaustive in nature. API makes no warranties, express or implied for reliance on or any omissions from the information contained in this document.

5.3.2 Analysis Reported in Mole Fraction

For compositional analysis that reports the composition in mole fractions, the equation to calculate carbon content is:

$$CC_{Mixture} = \frac{\sum_{i=1}^{\# \text{ of Components}} (n \times AW_{Carbon} \times Xm_i)}{\# \text{ of Components}}$$

$$\sum_{i=1}^{\# \text{ of Components}} (MW_i \times Xm_i)$$

where

CC_{Mixture} is the carbon content weight fraction of the mixture;

n is the number of carbon atoms in the component (e.g. for propane, C_3H_8 , *n* = 3);

AW_{Carbon} is the atomic weight of carbon;

MW_{*i*} is the molecular weight of component *i*;

 Xm_i is the mole fraction.

See Table 1 for an example carbon content calculation using a composition reported in mole fraction.

NOTE For compositional analysis reported in mole percent, convert the composition to mole fraction by dividing by 100.

Table 1—Example Carbon Content Calculation for a Fuel Mixture Reported in Mole Fraction

	Mole Fraction Xm	Molar Mass MW	No. of Carbon Atoms in the Component <i>n</i>	Atomic Weight of Carbon AW _{Carbon}	<i>n</i> × AW _{Carbon} × <i>Xm</i>	Xm × MW	
N ₂	0.0100	28.0134	0	12.011	0.000000	0.280134	
CO ₂	0.0200	44.0095	1	12.011	0.240220	0.880190	
CH ₄	0.9000	16.0425	1	12.011	10.809900	14.438250	
C ₂ H ₆	0.0500	30.0690	2	12.011	1.201100	1.503450	
C ₃ H ₈	0.0200	44.0596	3	12.011	0.720660	0.881192	
Total	Total 1.0000						
Sum of $(n \times AW_{Carbon} \times Xm)$ 12.9719							
Sum of $(Xm \times MW)$							
CC (carbon content mass fraction) = 12.9719/17.9832							

5.3.3 Analysis Reported in Mass Fractions

For compositional analysis that reports the composition in mass fractions, the equation to calculate carbon content is:

$$CC_{Mixture} = \sum_{i=1}^{\# \text{ of Components}} \left(\frac{n \times AW_{Carbon}}{MW_{Component}} \times Xw_i \right)$$

where

CC _{Mixture}	is the carbon content weight fraction of the mixture;
n	is the number of carbon atoms in the component (e.g. for propane, C_3H_8 , $n = 3$);
AW _{Carbon}	is the atomic weight of carbon;
MW _i	is the molecular weight of component <i>i</i> ;
Xw _i	is the mass fraction of each component.

See Table 2 for an example carbon content calculation using the same composition as given in Table 1 with the composition reported in mass fraction.

NOTE For compositional analysis reported in mass percent, convert the composition to mass fraction by dividing by 100.

Table 2—Example Carbon Content Calculation for a Fuel Mixture Reported in Mass Fraction

	Mole Fraction Xm	Molar Mass MW	No. of Carbon Atoms in the Component <i>n</i>	Atomic Weight of Carbon AW _{Carbon}	$\frac{n \times AW_{Carbon}}{MW_{Component}} \times Xw$
N ₂	0.0156	28.0134	0	12.011	0.000000
CO ₂	0.0489	44.0095	1	12.011	0.013358
CH ₄	0.8029	16.0425	1	12.011	0.601111
C ₂ H ₆	0.0836	30.0690	2	12.011	0.066790
C ₃ H ₈	0.0490	44.0596	3	12.011	0.040074
Total	1.0000				
CC (carbo	0.721				

5.4 Estimation of Carbon Content from Other Fuel Properties

Carbon content can also be estimated from other process or fuel supply properties. For example, heating value has been used to develop factors that are correlated to the fuel type and carbon content. The API *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry*^[5], August 2009, summarizes a number of these correlations with Table 3-8 providing carbon content and heating value information for a number of petroleum products that would not typically be analyzed by chromatographic methods for carbon content, and Table 3-9 providing this information for natural gas by heating value range.

Use of these correlation factors works well for compositions with limited variability or for fuel supplies where the heating value is continuously monitored or controlled. For example, if the fuel supply is natural gas and the supplier monitors the heating value by delivery zone, or the fuel supply is distillate oil (diesel) or fuel oil #4.

For process or fuel supplies with widely varying compositions or that are subject to periodic upset conditions, the frequency, duration, and carbon content of this variability needs to be characterized to accurately calculate the average carbon content. For process or fuel supplies where the carbon content is determined from sampling, the first reaction is to increase the sampling frequency. Increased sampling frequency only works if the composition change is normally distributed and a large number of samples are taken. Sample data taken from process or fuel supplies that are subject to upsets require, evaluation of the sample data and accounting for any upset samples by combining them with the average of the remaining samples using a weighting factor based on the frequency and duration of upsets.

An alternative method to solely increase the sampling frequency is to use an online measurement, as this method can be used to characterize the frequency and duration of composition changes against that of another correlative property. By combining the carbon content calculated from the measurement of this property and its carbon content correlation with sampling data, the accuracy of the average carbon content calculation can be improved. The heating value property has historically been used for this purpose, but this measurement is usually made with a chromatograph, which can be expensive and difficult to maintain. Correlation of carbon content to other gas properties used in the measurement process (e.g. density or speed of sound) may be a more viable correlation alternative. Annex A provides examples of estimating the correlation of process or fuel supply properties to carbon content, and Annex B provides examples of estimating the uncertainty of these correlations along with spot samples.

5.5 Calculation of Emissions

The API *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry* ^[5], August 2009, provides example calculations of CO₂, CH₄, and N₂O emissions.

6 Reporting Period Carbon Content Uncertainty

6.1 Objective

The purpose of this section is to provide an estimate of carbon content reporting period uncertainty based on multiple periodic samples taken at intervals that are independent of the process or fuel supply operation.

6.2 Reporting Period Carbon Content Calculated from Multiple Gas Samples

6.2.1 Average Carbon Content

The average carbon content can be calculated from the samples taken over the reporting period by:

$$CC_{Average} = \frac{\Sigma Sample Carbon Content}{Number of Samples}$$

where

CC _{Average}	is the reporting period average carbon content
Sample Carbon Content	is the carbon content of the sample;
Number of Samples	is the number of samples.

6.2.2 Average Carbon Content Expanded Uncertainty (95 % Confidence Level)

The 95 % confidence level carbon content uncertainty for the period that the average sample data is used can be calculated from the following equation:

Period CC_{95% Uncertainty} = $\pm \frac{k_{95\%} \times \sigma}{\sqrt{\text{Number of Samples}}}$

where

Period CC95% Uncertainty	is the period carbon content 95 % confidence uncertainty;
k95%	is the 95 % confidence coverage factor;
σ	is the carbon content standard deviation of the samples;
Number of Samples	is the number of samples.

The value of $k_{95\%}$ can be estimated from degrees of freedom as described in ISO/IEC Guide 98-3 (GUM) ^[33] and typically range from 2 (for a normal distribution with infinite degrees of freedom) to 3 (for distributions with very limited degrees of freedom). The $k_{95\%}$ values of 3 can be used for ease of calculation.

The percent period uncertainty can be calculated for the period uncertainty by:

% Period CC_{95% Uncertainty} =
$$\pm \frac{\text{Period CC}_{95\% \text{ Uncertainty}}}{\text{CC}_{\text{Average}}} \times 100$$

where

% Period CC_{95% Uncertainty} is the percent period carbon content 95 % confidence uncertainty;

Period CC_{95% Uncertainty} is the period carbon content 95 % confidence uncertainty;

CC_{Average} is the period average carbon content

EXAMPLE If the carbon content of 12 monthly samples is: 0.727, 0.737, 0.746, 0.725, 0.742, 0.734, 0.739, 0.747, 0.695, 0.728, 0.745, and 0.746 and an estimate of $k_{95\%}$ = 3 is used:

Sampling Period CC_{95% Uncertainty} =
$$\pm \frac{k_{95\%} \times \sigma}{\sqrt{\text{Number of Samples}}}$$

= $\pm \frac{3 \times 0.0147}{\sqrt{12}} = \pm 0.0127$
% Period CC_{95% Uncertainty} = $\pm \frac{\text{Sampling Period CC}_{95\% \text{Uncertainty}} \times 100$

$$= \pm \frac{0.0127}{0.734} \times 100 = 1.7$$

6.2.3 Number of Samples Required to Meet a Target Reporting Period Uncertainty

If one is interested in determining the number of samples required to meet an average carbon content uncertainty target, it can be calculated by the rearranged equation below. It is important to note that the evaluation of the uncertainty is based on estimates or previous results and it is assumed that the conditions of the measurement remain unchanged.

The number of samples required to meet a sample period average carbon content target uncertainty can be calculated by:

Number of Samples =
$$\left(\frac{k_{95\%} \times \sigma/CC_{\text{Average}} \times 100}{\text{Target Percent CC}_{\text{Uncertainty}}}\right)^2$$

where

Number of Samples	is the number of samples;
k95%	is the 95 % confidence coverage factor;
σ	is the carbon content standard deviation of the samples;
Target Percent CC _{Uncertainty}	is the target reporting period percent uncertainty.

EXAMPLE Using the 12 monthly carbon content example above, the $k_{95\%}$ is again estimated to be 3, the standard deviation is known to be 0.0147, and the average carbon content is 0.734. If the target carbon content uncertainty over the next reporting period is 5 %, then the number of samples required during the period is:

Number of Samples =
$$\left(\frac{k_{95\%} \times \sigma/CC_{Average} \times 100}{\text{Target Percent } CC_{\text{Uncertainty}}}\right)^2$$

= $\left[\frac{(3 \times 0.0147)/0.734 \times 100}{5}\right]^2$ = 1.2, which is a minimum of two samples.

Annex A (informative)

Estimation of Carbon Content Correlation to Fuel Properties

A.1 Single Composition Upset or Change

For process or fuel supplies that have a single component of composition that changes the average fuel composition, the correlation of carbon content to the fuel property can be estimated by:

- calculating the carbon content and fuel property for the average composition,
- calculating the carbon content and fuel property for the combined composition,
- calculating the linear trend of carbon content to fuel property between these two composition points.

For example, the carbon content to relative density correlation of a fuel source that can experience nitrogen upset of up to 10 % can be estimated by:

— average composition, carbon content, and relative density calculations (see Table A.1).

Mole %	Mole Fraction <i>Xm</i>	Molar Mass MW	No. of Carbon Atoms in the Component <i>n</i>	Atomic Weight of Carbon AW _{Carbon}	<i>n</i> × AW _{Carbon} × <i>Xm</i>	<i>Xm</i> × MW
Methane	0.8736	16.0425	1	12.0107	10.492659	14.014877
Nitrogen	0.0000	28.0134	0	12.0107	0.000000	0.000000
Carbon Dioxide	0.0371	44.0095	1	12.0107	0.445535	1.632524
Ethane	0.0136	30.0690	2	12.0107	0.327274	0.409669
Propane	0.0070	44.0956	3	12.0107	0.251008	0.307180
H ₂ O	0.0000	18.0153	0	12.0107	0.000000	0.000000
H ₂ S	0.0000	34.0809	0	12.0107	0.000000	0.000000
Hydrogen	0.0000	1.0079	0	12.0107	0.000000	0.000000
Carbon Monoxide	0.0000	28.0101	1	12.0107	0.000000	0.000000
Oxygen	0.0000	15.9994	0	12.0107	0.000000	0.000000
i-Butane	0.0010	58.1222	4	12.0107	0.049234	0.059563
n-Butane	0.0010	58.1222	4	12.0107	0.048926	0.059190
i-Pentane	0.0000	72.1488	5	12.0107	0.000000	0.000000
n-Pentane	0.0000	72.1488	5	12.0107	0.000000	0.000000
n-Hexane	0.0000	86.1754	6	12.0107	0.000000	0.000000
n-Heptane	0.0000	100.2019	7	12.0107	0.000000	0.000000
n-Octane	0.0000	114.2285	8	12.0107	0.000000	0.000000
n-Nonane	0.0000	128.2551	9	12.0107	0.000000	0.000000
n-Decane	0.0000	142.2817	10	12.0107	0.000000	0.000000
Helium	0.0667	4.0026	0	12.0107	0.000000	0.266822
Argon	0.0000	39.9480	0	12.0107	0.000000	0.000000
Total	1.0000					
Sum of $(n \times AW_{Carbon} \times Xm)$ 11.6146						
Sum of (Xm × MW)						
CC (carbon content mass fraction) = 11.6146/16.7498						0.6934
Relative Density (

Table A.1—Average Process Composition

 reducing each of the average composition components by 10 % and adding in 10 % nitrogen and recalculating the carbon content and relative density (see Table A.2);

Mole %	Mole Fraction <i>Xm</i>	Molar Mass MW	No. of Carbon Atoms in the Component <i>n</i>	Atomic Weight of Carbon AW _{Carbon}	<i>n</i> × AW _{Carbon} × <i>Xm</i>	Xm × MW
Methane	0.7862	16.0425	1	12.0107	9.443393	12.613390
Nitrogen	0.1000	28.0134	0	12.0107	0.000000	2.801340
Carbon Dioxide	0.0334	44.0095	1	12.0107	0.400981	1.469272
Ethane	0.0123	30.0690	2	12.0107	0.294547	0.368702
Propane	0.0063	44.0956	3	12.0107	0.225907	0.276462
H ₂ O	0.0000	18.0153	0	12.0107	0.000000	0.000000
H ₂ S	0.0000	34.0809	0	12.0107	0.000000	0.000000
Hydrogen	0.0000	1.0079	0	12.0107	0.000000	0.000000
Carbon Monoxide	0.0000	28.0101	1	12.0107	0.000000	0.000000
Oxygen	0.0000	15.9994	0	12.0107	0.000000	0.000000
i-Butane	0.0009	58.1222	4	12.0107	0.044310	0.053607
n-Butane	0.0009	58.1222	4	12.0107	0.044033	0.053271
i-Pentane	0.0000	72.1488	5	12.0107	0.000000	0.000000
n-Pentane	0.0000	72.1488	5	12.0107	0.000000	0.000000
n-Hexane	0.0000	86.1754	6	12.0107	0.000000	0.000000
n-Heptane	0.0000	100.2019	7	12.0107	0.000000	0.000000
n-Octane	0.0000	114.2285	8	12.0107	0.000000	0.000000
n-Nonane	0.0000	128.2551	9	12.0107	0.000000	0.000000
n-Decane	0.0000	142.2817	10	12.0107	0.000000	0.000000
Helium	0.0600	4.0026	0	12.0107	0.000000	0.240140
Argon	0.0000	39.9480	0	12.0107	0.000000	0.000000
Total	1.0000					
Sum of $(n \times AW_{Carbon} \times Xm)$ 10.4532						
Sum of ($Xm \times MW$)						
CC (carbon content mass fraction) = 10.4532/17.8762						
Relative Density						

plotting carbon content versus relative density and calculating the trend line (see Figure A.1).



Figure A.1—Calculated Carbon Content to Relative Density Correlation

The correlation between carbon content and relative density for this example is:

carbon content = $-2.7995 \times$ relative density + 2.3159

A.2 Monte Carlo Simulation

Monte Carlo simulation is a method that estimates possible outcomes by simulating a large number of random sets of variables and observing the outcomes. This technique can be used to simulate a large number of composition sets based on an average composition and normal distributions of the variability of each component. This data is used to calculate the carbon content and fuel properties which can then be used to calculate the correlation of carbon content to the fuel property.

For example, the carbon content to relative density correlation of a fuel source that can experience nitrogen upset of up to 10 % can be estimated as given in Section A.1 or can be estimated by Monte Carlo simulation. The carbon contents of the simulated compositions are shown in Figure A.2 and Figure A.3.



Figure A.2—Nitrogen Upset Fuel Carbon Content Calculated from Monte Carlo Simulation Results



Figure A.3—Nitrogen Upset Fuel Carbon Content vs Relative Density

The correlation between carbon content and relative density for this example is:

carbon content = $-2.8102 \times \text{relative density} + 2.32$

which is approximately the same correlation calculated in Section A.1 for the same conditions.

The real value of Monte Carlo simulation is not for this simple case, but for cases where there is variability in multiple components. Using Monte Carlo simulation will estimate the correlation as well as provide an estimate of the variability around the correlation. For example, if the process or fuel source shown in the previous examples could experience changes in the range of 0 % to 10 % nitrogen, 3.2 % to 5.2 % carbon dioxide, and 3.1 % to 13.1 % hydrogen, the Monte Carlo simulation would be as shown in Figure A.4 and Figure A.5.



Figure A.4—Multiple Component Variations Carbon Content Calculated from Monte Carlo Simulation



Figure A.5—Multiple Component Variations Fuel Carbon Content vs Relative Density

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Note that there is still a definite correlation between carbon content and relative density, but there is also uncertainty between the correlation and the process or fuel source carbon content. The sequential composition simulation has a mean carbon content of 0.629 with a deviation from the mean of ± 0.049 or ± 7.8 % (95 % confidence interval). The carbon content correlated to relative density has a deviation from the correlation trend line of ± 0.030 or ± 4.8 % (95 % confidence interval). It should also be noted, however, that the validity of the proposed Monte Carlo approach depends on the validity of the assumptions and appropriate sampling techniques in the simulation. In this case, there is an assumption of independence of components.

Annex B

(informative)

Estimation of Carbon Content Uncertainty

B.1 Fuel Carbon Content Uncertainty—Multiple Spot Samples

The uncertainty of reporting period fuel carbon content (e.g. its 95 % confidence interval) can also be reduced by using multiple fuel samples. Increasing the number of samples reduces the uncertainty of the reporting period average carbon content by the square root of the number of samples.

For example, if the fuel is:

- sampled monthly,
- the 12 spot samples carbon contents are averaged to determine the reporting period fuel carbon content,
- the composition is normally distributed, and
- the standard deviation of the 12 samples is 3.9 %,

then the 95 % confidence interval of the 12 samples would be $\pm (3 \times 3.9 \text{ \%})/\sqrt{12}$ or $\pm 3.4 \text{ \%}$.

However, if the composition is not normally distributed, for example, the process/fuel supply is subject to periodic upsets, then the statistical determination of the number of samples required to meet an uncertainty target changes.

B.2 Fuel Carbon Content Uncertainty—Relative Density and Multiple Spot Samples

Measurement of properties, such as relative density, can be used to estimate the frequency and duration of process or fuel supply variations. Calculation of carbon content from these properties can also be used to reduce the uncertainty of the process or fuel supply average carbon content, but process or fuel supply samples are still required to ensure that the simulated correlation maintains its relationship to process or fuel supply changes. By combining the fuel property to carbon content slope correlation calculated in accordance with Section A.1 or Section A.2 with spot samples to correlation offset data, an improved correlation can be calculated while minimizing the number of samples required to meet a target carbon content uncertainty.

This is accomplished by retaining the slope of the correlation calculated by either method and adjusting its offset with the sample data to obtain a property correlation that is based on the sample mixtures. By combining the slope correlation with the sample offset data, the simulation mixture estimates are shifted to align with real composition mixtures and the new combined correlation uncertainty is reduced. For Monte Carlo simulations this reduction can be estimated by dividing the original Monte Carlo simulation Uncertainty_{95%} by the square root of the number of samples.

For example, if the multiple component process or fuel supply variations Monte Carlo simulation from Figure A.5 was combined with four spot samples, then the correlation would be adjusted as shown below in Table B.1 and Figure B.1.

The uncertainty of the average carbon content calculated from the adjusted correlation could be estimated as:

Uncertainty₉₅ =
$$\frac{\text{Original Correlation Uncertainty}_{95}}{\sqrt{\text{Number of Samples}}} = \frac{\pm 4.8 \%}{\sqrt{4}} = \pm 2.4 \%$$

Spot Sample	Carbon Content	Relative Density	Carbon Content Calculated from Correlation	Sample to Correlation Carbon Content Difference
1	0.6111	0.5917	0.6352	-0.0241
2	0.6732	0.5885	0.6407	0.0325
3	0.6278	0.5882	0.6411	-0.0133
4	0.6544	0.6000	0.6212	0.0332
Average Carbon	0.0071			
Original Correlation	1.6378			
Adjusted Correlat	1.6449			







B.3 Validation of Fuel Carbon Content—Relative Density/Spot Sample Method

To validate the uncertainty estimate as calculated in Section B.2, the results of using spot samples and relative density/carbon content correlation obtained from a year's worth of hourly gas chromatograph data from four different refinery streams was used. By selecting the gas analysis from hour one of each reporting period as sample set one, the gas analysis from hour two of each reporting period as sample set two and so on until the last hour of the sample period was reached, multiple daily/weekly/monthly/quarterly spot sampling data sets were created. Using real data in this manner creates simulated data sets that are similar to using a Monte Carlo simulated data set and can be used to verify the estimated uncertainty calculated in Section B.2.

The resulting number and size of the sample sets are summarized in Table B.2.

Table	B.2-S	pot Sam	ple Sets
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Reporting Period	Number of Sample Sets/Stream	Number of Samples per Sample Set
Daily Spot Samples	24—one for each hour of the day	365
Weekly Spot Samples	168—one for each hour of the week	52
Monthly Spot Samples	720—one for each hour of the month	12
Quarterly Spot Samples	2880—one for each hour of the quarter	4

Table B.3 summarizes the stream compositions.

ę	Stream	H ₂ %	N ₂ %	CO %	CO ₂ %	C1 %	C2plus %
	Min	3.41	0.00	0.36	0.00	25.36	3.43
1	Max	51.67	0.00	17.49	0.64	87.06	33.60
	Average	29.33	0.00	10.15	0.28	48.03	12.21
	Min	20.50	0.00	0.53	0.03	22.90	3.72
2	Max	60.65	0.00	9.52	0.58	68.97	21.47
	Average	42.73	0.00	1.73	0.22	43.53	11.79
	Min	4.27	0.31	0.00	0.33	40.36	0.66
3	Max	55.91	2.10	3.65	1.61	92.39	5.63
	Average	37.32	0.63	0.17	0.84	59.80	1.24
	Min	12.72	0.57	0.13	0.00	23.02	12.68
4	Мах	56.24	6.18	2.04	0.41	68.86	35.83
	Average	26.85	4.09	1.08	0.09	43.08	24.80

Table	B.3—Strean	n Compositions
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For each stream and each sample data set,

- the composition without hydrogen was calculated from the average of each component for all of the samples in the data set. Zeroing the percent hydrogen and normalizing the resulting averages to 100 % allowed the zero hydrogen relative density and carbon content to be calculated;
- the maximum hydrogen composition was calculated for each sample set using the maximum hydrogen value of the sample set and normalizing it into the composition calculated in the previous step, allowing the second relative density and carbon content pair to be calculated;
- the relative density to carbon content slope and offset was then calculated from these two pairs of relative density/carbon content as shown in Section A.2;
- the slope and offset from each sample set was then used to calculate the carbon content for each hourly composition relative density. The offset of each sample set was adjusted to the average of the carbon content of the spot sample set as shown in Section B.2;
- the average carbon content calculated from relative density and the average carbon content of each sample set was then compared to the average carbon content of all of the hourly stream compositions.

Figure B.2 summarizes the results of the average carbon content calculated from each of the quarterly sample sets—2880 sets of compositions for each of the streams. The X axis shows the carbon content error from the combined sample and relative density calculation, and the Y axis shows the carbon content error from the sample alone and plotted point shows the intersection of these two errors for each sample set. The slope of the linear trend of these data point shows the relationship between the two carbon content estimation methods with a slope of 1.67, meaning the error on the Y axis is 1.67 times larger than the error on the X axis. The improvement in carbon content uncertainty is summarized in Table B.4.



Figure	B.2—Quarterly	Sampling and F	Relative Density	Calculations	Compared to	Quarterly	Sampling
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Table B.4—Summary	y of Improvement	in Annual Carbon	Content Determination
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	Approximate Improvement Using Sampling and Relative Density versus Sampling Alone
Stream 1	~3 %
Stream 2	~22 %
Stream 3	~67 %
Stream 4	~13 %

At first glance the obvious question is why is there almost no improvement in the carbon content calculated from relative density and sampling for Stream 1, and almost 70 % improvement for Stream 3. The answer lies in the deviation of the data around the carbon content to relative density correlation versus the deviation of the carbon content data itself.

The standard deviation and uncertainty data for the four streams is summarized in Table B.5. Notice that Uncertainty 95 % ($U^{95\%}$) for Stream 1 has a large overlap between the carbon content calculated from hourly composition (5 % to 7.5 %) and the carbon content calculated from relative density (4 % to 7.1 %). $U^{95\%}$ for Stream 3 has no overlap between the carbon content calculated from hourly composition: 2.6 % to 3.9 % and the carbon content calculated from relative density: 1.2 % to 1.7 %. The increased deviation in both the hourly carbon content and the relative density correlation of Stream 1 is caused by the large variability in carbon monoxide (0.4 % to 17.5 %) in addition to the large variability in hydrogen (3.4 % to 51.7 %) as shown in Table B.3. The effect of using the relative density or other correlation techniques to calculate carbon content for other fuel supplies can be estimated using Monte Carlo simulation.

	H	Hourly Carbon Content Calculated from Composition				Hourly Carbon Content Calculated from Composition			
	Standard Deviation %	Uncertainty U ^{95%} Using a Coverage Factor of 2 to 3 %	Quarterly Sampling Uncertainty %	Monthly Sampling %	Standard Deviation %	Uncertainty U ^{95%} Using a Coverage Factor of 2 to 3 %	Quarterly Sampling Uncertainty %	Monthly Sampling %	
Stream 1	2.5	5.0 to 7.5	2.5 to 3.8	1.4 to 2.2	2.0	4.0 to 6.1	2.0 to 3.0	1.2 to 1.8	
Stream 2	1.1	2.2 to 3.3	1.1 to 1.7	0.6 to 1.0	0.8	1.6 to 2.4	0.8 to 1.2	0.5 to 0.7	
Stream 3	1.3	2.6 to 3.9	1.3 to 2.0	0.8 to 1.1	0.6	1.2 to 1.7	0.6 to 0.9	0.3 to 0.5	
Stream 4	1.6	3.2 to 4.8	1.6 to 2.4	0.9 to 1.4	1.5	2.9 to 4.4	1.5 to 2.2	0.8 to 1.3	

For completeness, Figure B.3 has been included to show the same calculation data for monthly spot samples as the quarterly spot samples in Figure B.2, and Figure B.4 has been included to show the composition variability of each fuel stream.



Figure B.3—Monthly Sampling and Relative Density Calculations Compared to Monthly Sampling



Figure B.4—Composition Variability of the Four Fuel Streams

Bibliography

The documents listed below are NOT an exhaustive list of all standards relevant for the application of this TR. Furthermore, the list can only be used as a guideline and some of the references may not apply.

- [1] API Manual of Petroleum Measurement Standards (MPMS) Chapter 8.1, Manual Sampling of Petroleum and Petroleum Products
- [2] API MPMS Chapter 8.2, Automatic Sampling of Petroleum and Petroleum Products
- [3] API MPMS Chapter 8.3, Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
- [4] API MPMS Chapter 14.1, Collecting and Handling of Natural Gas Samples for Custody Transfer
- [5] API, Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry, August 2009, http://www.api.org/ehs/climate/new/upload/2009_GHG_COMPENDIUM.pdf
- [6] AGA Report No. 5¹, Natural Gas Energy Measurement
- [7] AGA Report No. 8, Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases
- [8] GPA 2103², Tentative Method for the Analysis of Natural Gas Condensate Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography
- [9] GPA 2145, Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry
- [10] GPA 2166, Obtaining Natural Gas Samples for Analysis by Gas Chromatography
- [11] GPA 2172, Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer
- [12] GPA 2174, Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography
- [13] GPA 2177, Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography
- [14] GPA 2186, Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography
- [15] GPA 2198, Selection, Preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends
- [16] GPA 2261, Analysis of Natural Gas and Similar Gaseous Mixtures by Gas Chromatography
- [17] GPA 2286, Tentative Method of Extended Analysis for Natural Gas and Similar Gaseous Mixtures by Temperature Programmed Gas Chromatography

¹ American Gas Association, 400 N. Capitol St., NW, Suite 450, Washington, DC 20001, www.aga.org.

² Gas Processors Association, 6526 E. 60th Street, Tulsa, Oklahoma 74145, www.gpaglobal.com.

- [18] GPA TP-17, Table of Physical Properties of Hydrocarbons for Extended Analysis of Natural Gases
- [19] ASTM D1070³, Standard Test Methods for Relative Density of Gaseous Fuels
- [20] ASTM D1265, Standard Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method)
- [21] ASTM D1945, Standard Test Method for Analysis of Natural Gas by Gas Chromatography
- [22] ASTM D2163, Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography
- [23] ASTM D3700, Standard Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
- [24] ASTM D4057, Standard Practice for Manual Sampling of Petroleum and Petroleum Products
- [25] ASTM D4177, Standard Practice for Automatic Sampling of Petroleum and Petroleum Products
- [26] ASTM D5134, Standard Test Method for Detailed Analysis of Petroleum Naphthas Through n-Nonane by Capillary Gas Chromatography
- [27] ASTM D5291, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
- [28] ASTM D5443, Standard Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multi-Dimensional Gas Chromatography
- [29] ASTM D6729, Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography
- [30] ASTM D7662, Standard Test Method for Carbon Content in Carbon Black Feedstock Oils
- [31] Federal Register, U.S. EPA, Part II: 40 CFR, Parts 51, 52, 70, et al. ⁴, Prevention of Significant Deterioration and Title V Greenhouse Gas Tailoring Rule; Proposed Rule—Tuesday October 27, 2009
- [32] Federal Register, U.S. EPA, Part II: 40 CFR, Parts 86, 87, 89, et al., Mandatory Reporting of Greenhouse Gases, Final Rule—Friday October 30, 2009
- [33] ISO/IEC Guide 98-3:2008 ⁵, Uncertainty of measurement—Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)

³ ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428, www.astm.org.

⁴ U.S. Environmental Protection Agency, Ariel Rios Building, 1200 Pennsylvania Avenue, NW, Washington, DC 20460, www.epa.gov.

⁵ International Organization for Standardization, 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, www.iso.org.

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