

**Preparation of Natural Gas Blends Used as Calibration Standards:
Sources of Uncertainty and Best Preparation Practices**

FINAL REPORT

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1.0 Introduction

1.1 Scope of This Report

This report presents the results of research designed to evaluate, document, and upgrade natural gas sampling technology, as directed and supervised by the American Petroleum Institute (API) Manual of Petroleum Measurement Standards (MPMS), Chapter 14.1 Gas Sampling Project Working Group. The project was created by the Measurement Technical Committee of the U.S. natural gas industry, and was funded jointly by the Gas Research Institute* (GRI) and the Minerals Management Service (MMS), U.S. Department of the Interior. Southwest Research Institute was contracted to perform this research, as part of a multi-year program in support of the revision of API MPMS Chapter 14.1, Collecting and Handling of Natural Gas Samples for Custody Transfer (Reference 1).

Five individual tasks were included in the 2002 study:

1. Comparative evaluation of equation-of-state models and characterization methods for determining the hydrocarbon dew point of a natural gas stream.
2. An evaluation of the fill-and-empty sampling method as a self-heating method when equipment temperature is below the hydrocarbon dew point.
3. Development of a performance verification test protocol for new gas sampling methods.
4. A review of the current state and direction of gas sampling research under saturated and wet gas conditions.
5. A review of methods for preparing natural gas blends used as calibration standards for chromatography equipment.

The last two research tasks were co-funded by the Minerals Management Service. This report presents the findings of the fifth task, a review of common methods of preparing reference gas standards. The review discusses techniques used by commercial gas blenders, the accuracy achievable in certified gases, sources of potential uncertainty, and “best practices” recommended for companies that supply calibration standards to the natural gas industry.

A separate report (Reference 2) presents a review of the state of the art of gas sampling techniques under wet gas conditions, the fourth task of the 2002 project. This report and Reference 2 serve as final deliverables for the research tasks co-funded by MMS during 2002. A GRI Topical Report (Reference 3) contains the findings of all five tasks conducted during the year.

1.2 Survey Participation

As part of the research task reported here, Southwest Research Institute conducted a survey of companies that prepare chromatographic calibration or reference natural gas blends or standards for the natural gas industry. The survey asked participants to report on their sources of stock materials, preparation methods and equipment, final composition uncertainties, and regulatory compliance. The purpose of the survey was to document the methods used to prepare chromatographic calibration gases or reference gas standards, and to establish achievable uncertainties for such gas compositions. The information from the survey may also be used to prepare future revisions of API MPMS Chapter 14.1.

* In April 2000, Gas Research Institute (GRI) and the Institute of Gas Technology (IGT) combined to form Gas Technology Institute (GTI).

SwRI asked seven companies that prepare reference gases to participate in the survey, and obtained responses from five of the seven companies. SwRI personnel also visited two of the preparation companies to observe their blending procedures and facilities firsthand, and to obtain a clearer understanding of potential pitfalls and improvements to the preparation process. From this information, SwRI also selected a company to provide reference gases for use in the hydrocarbon dew point experiments reported in Reference 3.

To encourage participation in the survey, it was agreed that no information would be identified with the company providing it. However, SwRI would like to thank the participants for supporting the Chapter 14.1 Working Group in their revision of API MPMS Chapter 14.1:

- Air Liquide Specialty Gases, LaPorte, TX, USA
- DCG Partnership I, Pearland, TX, USA
- EffectTech Ltd., Uttoxeter, Staffordshire, UK
- Gas Technology Institute, Des Plaines, IL, USA
- Scott Specialty Gases, Longmont, CO, USA.

2.0 The Need for Accuracy in Calibration Gas Blends

In the natural gas transmission industry, gas chromatographs (GCs) are regularly used to analyze natural gas samples drawn from transmission pipelines. The primary purpose of GC analyses is to determine the heating value and density of the natural gas. Many consider this the most important purpose of GC analysis, since the heating value of the gas, combined with the measured volumetric flow rate, determine its value for custody transfer. Another gas property that is determined using GC analyses is the dew point temperature, that is, the temperature at which hydrocarbon constituents or water vapor in the gas blend condense from the stream and begin to form liquids.

Precision uncertainties and biases in analytical compositions will cause inaccuracies in calculated properties of natural gas. As an example of the financial impact of such inaccuracies, consider a natural gas transmission stream flowing at 100 million standard cubic feet per day (MMSCFD), with a heating value of 1,000 Btu per standard cubic foot (Btu/scf). At \$4 per million Btu, the gas is worth \$400,000 per day. An error in heating value of 0.5% caused by inaccurate analysis will result in a custody transfer error of \$2,000 per day, or \$730,000 per year. In a case where a GC analysis is used to compute dew points, a gas supplier could be “shut in” for providing a gas stream that appears to have a dew point temperature that is higher than the actual value, resulting in unnecessary expenses to the companies that sell and transport natural gas.

2.1 Effect of GC Accuracy on Computed Dew Points

Some research has been performed on the accuracy of gas chromatography as it relates to dew point determination (References 4 and 5). Warner *et al.* (Reference 4) noted that routine analysis was only capable of quantifying hydrocarbon constituents from C₁ through C₆ until the mid-1980s, when advances in column technology made extended analyses to higher carbon numbers possible. The mole fraction of each isomer present in a natural gas blend generally decreases as the carbon number increases. Even with advanced GC technology, extended-analysis GCs must measure small amounts of heptane, octane, and heavier hydrocarbon constituents that can approach the limits of measurement resolution, and will carry large relative uncertainties. In their study of analytical accuracy, Warner *et al.* reported that variations in C₆₊ content on the order of 0.1 to 0.2 mol % typically led to variations in computed hydrocarbon dew point temperatures of 30 to 40°F.

More recent work by Cowper (Reference 5) included an example calculation of uncertainties in hydrocarbon dew points. A Monte Carlo technique was used to generate a large number of random natural gas compositions from a sample gas composition, using uncertainties in the sample composition, data on GC accuracy, and uncertainties in GC relative responses to heavier hydrocarbons. Dew points were then computed for the random compositions to assess the effects of the uncertainties. In the example, the uncertainty in computed dew point temperature due to uncertainties in composition was reported as 0.5°F, but the work assumed that hydrocarbons down through C₁₂ could be measured to within 0.1 parts per million (ppm).

Although extended analyses to C₁₄ are now possible in laboratories, and the level of resolution reported by Cowper may be achievable, such accuracy is not currently possible for process analyzers in the field. This is reflected in the current analysis procedure published by the Gas Processors Association (GPA) (Reference 6), which is tailored to C₆₊ analysis and is commonly followed in field applications for computing heating values rather than dew points. An ISO document now being drafted will serve as a standard for the accuracy of laboratory GC analyses in computing dew points and other gas properties, but no such document has been planned for process GC analyses.

2.2 Effect of GC Accuracy on Computed Heating Values

No information has been found in the open literature on the effects of GC analytical accuracy on computed heating values. However, these effects can be estimated using heating value data from GPA standards and gas densities computed by commercial software. Calculations performed for this report show that an error of 0.1 mol % in the analytical hexane content or C₆₊ fraction can lead to fiscally significant custody transfer errors.

Calculated heating values for several gas compositions are reported in Table 1. The table includes heating values for two certified gas compositions with nominal heating values of 1050 and 1520 Btu/scf. These certified compositions are of reference gases used in the hydrocarbon dew point experiments reported in Reference 3, but for this example, the certified compositions are treated as results of GC analyses. The certified compositions were then modified to simulate two different types of analytical errors.

- 1) One modification simulated an error in the analytical hexane content of 0.1 mol %. For the 1050 Btu/scf gas, the original, “analytical” hexane content was increased by 0.1 mol %. The other components were renormalized proportionately to return the total to 100 mol %. For the 1520 Btu/scf gas, hexane was both increased and decreased by 0.1 mol % from the “analytical” value, and the other components were renormalized to a total of 100 mol %.
- 2) The original compositions were also modified to simulate errors of ± 0.1 mol % in a lumped C₆₊ fraction. Changes in individual C₆₊ components were made, proportional to their original “analytical” values, so that the change in the total of hexane and heavier components was ± 0.1 mol %. The other components were renormalized proportionately to return the total to 100 mol %.

Heating value data for the gas components were taken from GPA Standard 2145-03 (Reference 7) and GPA Technical Publication TP-17 (Reference 8). Densities of the various gases at standard temperature and pressure (60°F, 14.696 psia) were computed using the Multiflash software package (Reference 9).

Table 1. Effects of errors in analytical values of hexane and lumped C₆₊ fraction on computed heating values. Concentrations “corrected for errors” are in bold type.

Component	1050 Btu/scf gas			1523 Btu/scf gas				
	as analyzed	after correction:		as analyzed	after correction:			
		hexane 0.1 mol% low	C ₆₊ fraction 0.1 mol% low		hexane 0.1 mol% high	hexane 0.1 mol% low	C ₆₊ fraction 0.1 mol% high	C ₆₊ fraction 0.1 mol% low
methane	94.737%	94.642%	94.642%	65.601%	65.667%	65.535%	65.667%	65.535%
ethane	2.022%	2.020%	2.020%	10.201%	10.211%	10.191%	10.211%	10.191%
propane	0.746%	0.745%	0.745%	7.884%	7.892%	7.876%	7.892%	7.876%
i-butane	0.299%	0.299%	0.299%	2.097%	2.099%	2.095%	2.099%	2.095%
n-butane	0.302%	0.302%	0.302%	6.205%	6.211%	6.199%	6.211%	6.199%
i-pentane	0.151%	0.151%	0.151%	1.806%	1.808%	1.804%	1.808%	1.804%
n-pentane	0.150%	0.150%	0.150%	2.202%	2.204%	2.200%	2.204%	2.200%
2,2-dimethylbutane	0.001%	0.001%	0.004%					
2-methylpentane	0.016%	0.016%	0.031%					
2,3-dimethylbutane	0.002%	0.002%	0.008%					
3-methylpentane	0.006%	0.006%	0.016%					
n-hexane	0.032%	0.132%	0.054%	0.383%	0.283%	0.483%	0.353%	0.413%
methylcyclopentane	0.001%	0.001%	0.006%					
benzene				0.100%	0.100%	0.100%	0.085%	0.115%
n-heptane	0.030%	0.030%	0.051%	0.135%	0.135%	0.135%	0.117%	0.153%
methylcyclohexane	0.000%	0.000%	0.001%					
toluene				0.100%	0.100%	0.100%	0.085%	0.115%
n-octane	0.009%	0.009%	0.020%	0.060%	0.060%	0.060%	0.048%	0.072%
n-nonane	0.001%	0.001%	0.006%	0.015%	0.015%	0.015%	0.009%	0.021%
n-decane	0.001%	0.001%	0.005%	0.007%	0.007%	0.007%	0.003%	0.011%
carbon dioxide	0.501%	0.500%	0.500%	1.201%	1.202%	1.200%	1.202%	1.200%
nitrogen	0.993%	0.992%	0.992%	2.003%	2.005%	2.001%	2.005%	2.001%
total	100.000%	100.000%	100.000%	100.000%	100.000%	100.000%	100.000%	100.000%
C ₆₊ fraction	0.0990%	0.1989%	0.1990%	0.8000%	0.7004%	0.8996%	0.7000%	0.9000%
heating value (Btu/lb _m)	23000.85	22990.64	22988.75	21561.90	21563.91	21559.90	21567.06	21556.77
density at 60°F, 14.696 psia (lb _m /scf)	0.04570	0.04588	0.04591	0.07056	0.07040	0.07072	0.07037	0.07075
heating value (Btu/scf)	1051.12	1054.86	1055.39	1521.40	1518.08	1524.72	1517.69	1525.11
error in analytical value (Btu/scf)		-3.74	-4.27		3.32	-3.32	3.71	-3.71

For the 1050 Btu/scf gas, an error of 0.1 mol % in the analytical lumped C₆₊ fraction causes a larger error in heating value than an error in the hexane content alone. This difference is noteworthy, because process GC analyzers in the field more commonly measure the lumped fraction than the individual constituents. Under the assumption that the GC analysis undermeasures the lumped C₆₊ fraction by 0.1 mol %, the analysis would produce a heating value of 1051.12 Btu/scf, whereas the gas would have an actual heating value of 1055.39 Btu/scf. The analysis would therefore lead to an error in heating value of -4.27 Btu/scf, or -0.4% of value. For the example pipeline at the beginning of this chapter flowing at 100 MMSCFD, this translates into a custody transfer error of \$1,600 per day, or \$584,000 per year. For the 1520 Btu/scf gas, an error of ±0.1 mol % in the analytical lumped C₆₊ fraction is again the worst case. This magnitude of measurement error would lead to a heating value that is off by ±3.71 Btu/scf, or ±0.24% in value, and would cause a custody transfer error in the example pipeline of slightly over \$350,000 per year.

2.3 Conclusions

This chapter has demonstrated the magnitude of errors in custody transfer and dew point calculations that can occur from errors in measured C₆₊ fractions on the order of ±0.1 mol %. Accurate measurements of heavy hydrocarbons to these levels, and calculation of accurate gas properties from GC analyses, require calibration gases with compositions certified to appropriate levels of accuracy. Large uncertainties in the heavier components introduce the potential for errors in GC calibration, specifically by biasing the computed response factors for those components. However, Warner *et al.* (Reference 4) noted at the time that few certified gas standards were available that contained ppm levels of C₉ and heavier components.

During the work to revise API MPMS Chapter 14.1, the Chapter 14.1 Working Group concluded that uncertainties in gravimetrically prepared calibration gases, and their impact on analytical accuracy, are not considered by most GC users. The survey of preparation companies reported here was commissioned by the Working Group to establish the uncertainties in currently available reference gases, and to identify “best practices” of preparation companies that can potentially reduce these uncertainties. With this information, it will be possible for users to assess the uncertainties in heating values, dew point temperatures, gas density, and other information derived from process analyses of natural gas blends. It may also be possible for gas blenders to improve their processes by following the recommendations of this report, and to prepare gases with tighter uncertainties suitable for their intended purpose.

3.0 Equipment and Materials Used in Reference Gas Preparation

This chapter reviews the findings of the survey in the areas of (1) the equipment used in gas blend preparation and (2) the purity, storage, and handling of raw materials. The next chapter discusses the preparation procedures themselves. In both chapters, recommended practices for improving blending procedures or composition accuracy are highlighted by arrows in the text. These recommendations are reiterated in the conclusions.

The initial survey of participants concentrated on gas preparation methods and equipment and composition uncertainties. The second survey was tailored to each respondent to clarify data from the first survey, and also focused on criteria related to the preparation of reference gases for SwRI hydrocarbon dew point experiments described in Reference 3. Copies of the initial and follow-up surveys can be found in the appendix.

3.1 Storage and Process Equipment

Earlier research on natural gas sample handling (References 10 and 11) has identified several causes of distortion in natural gas sample composition. Adsorption of components onto plastic tubing or into porous surfaces can change the composition of a natural gas mixture. Joule-Thomson cooling through valves and other temperature changes can cause condensation or vaporization of the heavy components. This may also lead to problems in transferring certain pure components to the recipient cylinder during blending, if gravimetric methods are not used to measure the amount of the component added. The effectiveness of equipment cleaning methods varies widely, and poorly cleaned equipment can contaminate hydrocarbon gases and liquids handled later with the same equipment.

Recognizing that causes of sample distortion may also corrupt blended reference gases, parts of the survey asked respondents to describe the equipment used to store and transfer raw materials and final products. Questions about cleaning methods were also posed to the participants. The following three subsections report on the survey findings in these areas.

3.1.1 Raw Material Containers

Each company was asked to describe the containers used to store raw materials and stock gases. All the respondents reported using constant-volume cylinders of various pressure ratings and sizes as containers for stock hydrocarbon gases. Aluminum or carbon steel were the most common materials for these cylinders, both of which have been found to have a low affinity for adsorbing hydrocarbons when properly prepared and maintained. For stocks of liquid hydrocarbons and volatile liquids, glass bottles or low-pressure aluminum or steel cylinders were more common among the five respondents. Less common containers for raw material storage, reported by one or two companies, included constant-pressure stainless steel cylinders, five-gallon cans, vials and ampoules. One company reported that it stores hydrocarbon liquids with low vapor pressures in 55-gallon carbon steel drums. (Use of such drums may require precautions to prevent rust or contamination of the contents.) Another company consistently uses cryogenic vessels for large volumes of hydrogen, nitrogen, argon, and carbon dioxide.

Some procedures were described that are listed here as recommended practices:

- ⇒ One respondent noted that container materials are checked for compatibility with their intended contents before use.
- ⇒ One respondent uses refrigerated storage to stabilize volatile raw materials.

3.1.2 Pressure and Flow Regulation Equipment

Each respondent was asked to describe the types of pressure and flow regulation devices used to dispense raw materials. Again, stainless steel was reported to be a common material in this equipment. Stainless steel valves are common to the majority of companies, and single-stage or double-stage regulators are commonly made of brass or stainless steel. At least two companies reported that they employ stainless steel needle valves. Although any device that causes a pressure reduction can expose heavier hydrocarbon streams to condensation through Joule-Thomson cooling, needle valves are potentially worse than regulators or other valve types in this regard. Also, needle valves can be prone to leaks and may not function well as shutoff valves. On the other hand, needle valves have less surface area for adsorption of heavy hydrocarbons, which is another loss mechanism. Ball valves were less common devices among the five companies surveyed. One respondent noted that their equipment includes only control valves and piping, apparently without needle valves. The same respondent also uses separate lines for each material and follows purging procedures to avoid cross-contamination of transfer equipment.

The material used in valve seals must also be chosen to avoid absorption of hydrocarbons. One respondent reported using only Viton, Kalrez or Buna-N seals in its equipment. Viton, in particular, is recommended among natural gas equipment companies for use with hydrocarbons. Another company specifically avoids neoprene seals.

3.1.3 Equipment Cleaning Methods

Participants were asked to describe their methods for cleaning and preparing raw material containers, valves, regulators, and containers used to transfer raw materials to the blending container. Responses varied among the companies, possibly due to different experiences with contamination. Some participants reported that they use water-based cleansers, others use inert gases, while still others use heat and vacuum instead of chemicals. Some participants disassemble and clean valves before reusing them. While this may be time-consuming, the advantages may outweigh the time required, depending on the previous material handled by the valve.

The descriptions of cleaning methods that follow are quoted from the survey responses.

- “No ‘cleaning agents’ are used. Passivation and vacuum/bake procedures are followed for cylinders containing stock gases and mixtures. Vacuum is also used to clean regulators prior to use.”
- “A water-based cleansing agent is used to remove traces of machine oils and other hydrocarbons from raw material containers prior to use and after hydrostatic retesting. Cylinders are then prepared by drying with acetone, baking under vacuum, purging with helium, and passivating cylinders with the raw material.”
- “Regulators are bought clean and assembled in a clean room. Syringes are cleaned using a heated vacuum syringe cleaner. Balances are equipped with static dissipaters.”
- “Internal cylinder cleaning uses proprietary processes. External surfaces are cleaned with a soft brush and ethanol to remove dirt and loose paint that may affect weighing processes. Wetted parts of regulators and needle valves are dismantled and any hydrocarbon grease residue is removed with a soft cloth, then a two-stage ultrasonic bath process (Genklene and acetone) is used to remove the remaining lubricant.”
- “New cylinders are rinsed with pesticide-grade hexane, rolled on their side for 1/2 hour, drained, and blown dry and odor-free with ultra-high purity nitrogen. Valves are then installed, and the cylinder is evacuated overnight. Regulators are purchased as high-purity

units, and no cleaning is performed. New valves are dismantled; stem threads are cleaned of excess lubricant, bodies are rinsed with hexane, blown dry with nitrogen, and reassembled.”

- “Containers are purged with an inert gas, then with the raw material that will occupy the container.”

In previous research, Behring (Reference 11) tested several different cleaning methods on constant-volume and constant-pressure natural gas sample cylinders. The tests were performed on cylinders contaminated with a mixture of equal parts C₆-C₁₀ normal hydrocarbons and SAE-30 compressor oil. Eight cleaning methods in all were tested, including some similar to the methods listed above: acetone, cleaning agents diluted in water, liquid propane, evacuation, and nitrogen and methane purges. Overall, flowing wet steam proved to be the most effective in removing hydrocarbon contamination and liquid residue from constant-volume cylinders. For constant-pressure cylinders, which also require cleaning between uses, the best results were obtained when the metal parts were disassembled, steam cleaned, and reassembled with new seals and Krytox lubricant. Behring noted that these results were also applicable to sample lines and fittings; however, none of the respondents to the survey used wet steam as a cleaning agent in their work.

During site visits to two of the gas preparation companies, further observations were made of equipment cleaning and preparation methods. After receiving raw materials such as methane or propane, both companies transfer the raw materials to standard cylinders for interim storage. A common preparation process for the interim storage cylinders is “vacuum baking:” heating the cylinders as a vacuum is drawn on the inside. This process works to remove contamination from the walls before the cylinders receive new raw materials. Details of this “vacuum bake” process can differ. One company heats the cylinders for one hour, while the other heats them overnight. One site also flushes the interim storage cylinders with nitrogen before the vacuum bake, and passivates the cylinders afterward using the reactive gas (or reactive components of the gas blend) that the storage cylinder will hold next.

Some procedures with the potential to introduce excess amounts of raw materials into the final blend were observed at both sites. However, steps are taken to remove this excess material before it enters the recipient blending cylinder. For example, a single syringe is used repeatedly to transfer successive liquid components into the recipient cylinder. After each component is transferred from the syringe, vacuum is applied to the syringe to draw leftover liquid out and avoid contaminating the next component with the previous component. The same vacuum step is used for small sample cylinders used to transfer lesser amounts of gases into the recipient cylinder. After one component is added to the recipient cylinder, vacuum pressure removes any remaining gas from the transfer cylinder before the next component is transferred in. One preparation company also uses the next component to “flush” the previous component from the small gas cylinder in some cases.

3.2 Source Materials

The purity of raw materials used to create the final blend influences the accuracy of certified gas compositions. Lower purity source materials contain higher amounts of impurities that can alter the final blend. Methane and ethane are normally held to higher standards of purity, because they make up a large portion of most gases and can potentially introduce the largest amounts of unwanted components as impurities.

The companies in the survey were asked to list their requirements for purity of raw materials. All companies reported their criteria for new raw materials, but not all of these criteria were absolute numbers. One company sets minimum purity limits ranging from 99.999% for methane down to 99% or better for n-hexane, but will use higher grades of raw materials if required by their customers. Another simply reported a minimum purity for raw materials of 99%, without specifying if lighter hydrocarbons must meet higher purities. A third company listed their requirements as “ultra-high-purity or better stock

gases and high purity liquids.” Numerical purity values are preferable to these terms, since definitions of “high purity” and “ultra-high purity” vary from one raw material provider to another. Of the other two companies, one bases their purity criteria on customer specifications, while the other simply uses the highest purity source materials available. While the highest available purity of hydrocarbon components can vary from time to time and from one supplier to another, this criterion would be expected to yield the smallest uncertainties in composition in the final blend.

Changes in the purity of raw materials over time are typically detected through GC analysis. Three of the five companies reported that they routinely analyze raw materials by GC before use. Two of the five companies reported that they screen raw materials routinely or at predefined intervals over the life of the supply. Two respondents stated that if GC analysis of a raw material shows a deviation from gravimetric values or specifications, the material is quarantined and no longer used. Another company sets aside raw materials that show increasing amounts of impurities, and uses them only when “small amounts” are required. One respondent follows procedures to deal with non-homogeneous distributions of impurities, such as headspace compositions of two-phase components. These are considered “short-term purity issues” by the company, and are accounted for in the certified composition of the final blend.

Several reasons for replacing raw materials were reported, and some preparation companies have more than one criterion for obtaining new batches of raw materials. The reasons listed in the survey, and the number of companies citing them, were as follows:

- Analysis shows raw materials are outside specifications (4 responses)
- Depletion of supply (2 responses)
- Expiration date/shelf life exceeded (2 responses)
- Usage rates (1 response; this either refers to a lower than usual usage rate, or refers to a method of ordering new supplies before existing supplies are depleted)
- “Fitness for purpose; high-purity gas or liquid with increasing impurities is relegated to use only when small amounts are required.” (1 response)

It should be noted that mixing old and new quantities of raw materials is not a generally accepted practice. Only one of five companies adds new lots of materials to old, and only with cryogenic gases and refrigerated CO₂. The other four do not follow this procedure with any raw materials.

4.0 Reference Gas Preparation Practices

This chapter reviews the procedures that companies follow in preparing gas blends. Much of the data collected during the surveys concerned the gas preparation process, and a greater understanding of the process was obtained during site visits to two of the participating companies. Several of the “best practices” listed in this chapter are only followed by one or two of the survey participants, but are recognized for their potential to improve accuracy in certified gas blends.

Participants provided information on all steps in their preparation process, and on the entire path followed by each component from the storage vessel to the recipient cylinder for the blend. Two companies use preparation methods written by the International Organization for Standardization (ISO) as guidelines. Others use written laboratory procedures to prepare gases, or describe their guidelines as “good laboratory practices.” General descriptions of the process followed by each company show that the details vary, but the general principles are similar.

- One company described their process as a “cascading” method, in which gases are transferred through stainless steel lines into stainless steel cylinders, and syringes are used for liquids. Required amounts for gravimetric blends are computed by a proprietary program, and measured using balances.
- Another company performs gravimetric preparation per standard ISO 6142 (Reference 12). Final products are prepared in aluminum cylinders (for gases with low sulfur content) or stainless cylinders (for high sulfur gases). Required amounts are computed using gas laws and compressibility data, and measured using high precision balances.
- Another company uses tubing or piping to transfer gases from separate sources (storage locations) to high-pressure cylinders. The final amounts added are determined using balances, if balance accuracy will allow the amounts to be measured to within $\pm 1\%$ of reading. For smaller amounts, the final composition is determined by chromatographic analysis.
- Another company transfers the most commonly used raw materials from remote storage to a “distribution panel” at the blending station, with valves and instrumentation located on the panel itself. Other gases are transferred using high-pressure transfer cylinders brought to the blending station, while liquids are injected into the recipient cylinder using syringes. Amounts to be added are computed using the ideal gas law, and final amounts are measured using analytical balances.
- The fifth company reported that raw materials are transferred by tubing, regulators, syringes and valves to gas cylinders. The required amounts are found using computer algorithms and spreadsheets, and then measured by syringe volumes, balances and pressure gauges. The final certification of the blend is performed by gas chromatography.

4.1 Regulatory Compliance

Each company was asked to list all government agencies whose regulations they must comply with, or industry standards that they follow. All companies within the United States use cylinders approved by the U.S. Department of Transportation (D.O.T.), and test them as required to comply with D.O.T. regulations. Companies outside the U.S. use similarly approved equipment rated by their own government. Some companies in the survey listed compliance with other agencies, including:

- U.S. Environmental Protection Agency (EPA)
- U.S. Department of Labor, Occupational Safety and Health Administration (OSHA)

- Texas Railroad Commission (this agency regulates the oil and natural gas industry in Texas)
- ASTM International (formerly the American Society for Testing and Materials)
- American National Standards Institute (ANSI)
- Gas Processors Association (GPA)
- Compressed Gas Association (CGA)

One company uses internal and external audits to ensure compliance with appropriate organizations, while another maintains regular compliance records on site and trains personnel regularly to comply with government guidelines. The majority of companies leak-test valves, syringes, and transfer lines as part of their compliance with regulations.

4.2 Procurement, Storage and Transfer of Raw Materials

Much of the detail about the quality of raw materials and their storage was obtained from site visits to two of the five companies. One site obtains raw materials from a variety of sources, while the other obtains nearly all of their stock material from a single source. Using several different sources can have advantages. For example, if one supplier experiences problems with product purity, work can continue with pure gases from other suppliers. Two procedures observed at both locations are listed as recommended practices:

- ⇒ Both sites perform GC analyses on raw materials to check for impurities.
- ⇒ Both sites use the uncertainties in raw materials stated by suppliers, and/or the analytical impurities measured by GC, in generating certified compositions of their final products.

One site specifically performs a GC check on the first batch transferred from the delivery vessel to interim storage cylinders.

Both sites prepare their blends in climate-controlled or air-conditioned rooms, but store large amounts of gaseous raw materials in large loading docks or buildings open to the outside. This poses minimal problems for gases with very low condensation temperatures, such as methane. However, for pure gases that could condense when stored outside under the right combination of conditions, outside storage should be considered carefully, and avoided if unnecessary.

- ⇒ If it is necessary to change the raw material held by a storage cylinder, both sites perform the “change-in-service” in accordance with CGA guidelines. The handling of storage cylinders according to CGA guidelines is a recommended practice.

One site also sorts their storage cylinders according to CGA number, to help in the process of storing gases in cylinders of compatible materials. One facility manually monitors the pressure in each storage cylinder to avoid backflow of air into the bottle and total exhaustion of the cylinder. The other facility fits their storage cylinders with reverse pressure valves that stop all flow when internal pressure reaches a preset level. These reverse pressure valves eliminate the need for pressure or temperature gauges.

4.3 Pre-Blend Calculations

As noted above, methods of computing the mass of each component to be added range from the ideal gas law, to spreadsheets, to proprietary software built around equations of state developed from experimental data. Both sites visited by SwRI staff use computers and equations of state, which are considered the fastest and most accurate method. One site uses a combination of proprietary and commercial software to compute (1) the mass of each component to be added to a blend, (2) the delivery

pressure, and (3) the blend dew point. The other site uses a single program to perform all calculations, but delivers the same information.

Both use data from GPA and Gas Processors Suppliers Association (GPSA) standards for the properties of each component. However, the two sets of software use different equations of state (Peng-Robinson versus Redlich-Kwong). As noted in Reference 3, dew points predicted by the Peng-Robinson equation and the Soave-Redlich-Kwong equation (a successor to the Redlich-Kwong equation) can vary by 10°F. For nominally identical gases, similar variations could be expected in pre-blend calculations of dew point by the two sites, because of differences in equations, property data, or calculational methods. Variations in minimum delivery pressure would be expected for the same reasons.

4.4 Blending Procedures

Figure 1 shows a typical setup for preparing a certified gas blend. The key piece of equipment is a “transfer assembly,” which is shown as a horizontal tube with fittings at both ends and a third fitting extending from the middle. These connect the assembly to (1) the diaphragm valve on the cylinder in which the blend is prepared; (2) a vacuum line, which removes residual gases from the assembly before each component is added; and (3) a transfer cylinder that contains the desired amount of a single component to be added to the blend. The blending process begins with the recipient cylinder under vacuum to draw in materials from the transfer cylinders or syringe. The recipient cylinders have diaphragm valves of the type described in Section 3.1.2. One participant specifically uses diaphragm

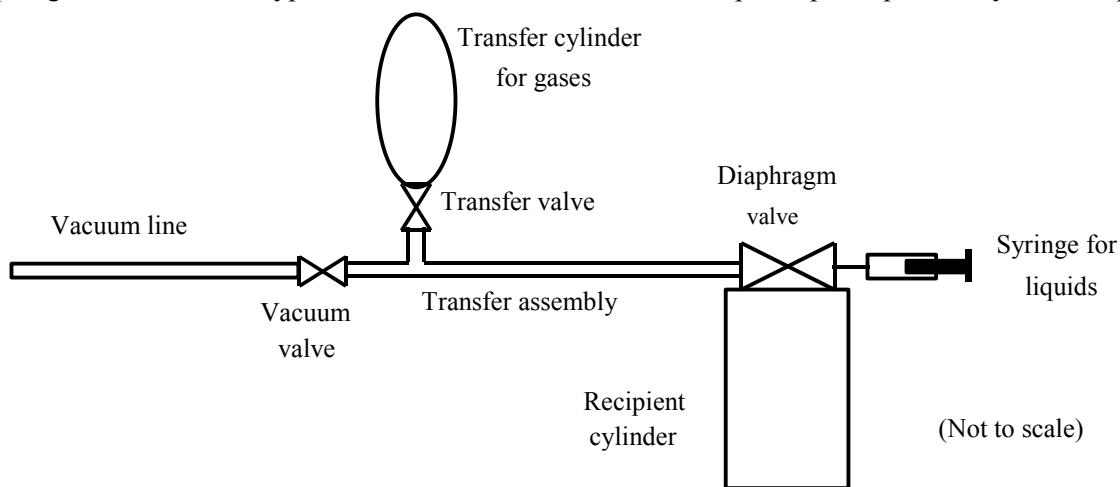


Figure 1. Example of a setup for preparing a certified gas blend.

cylinder valves on the recipient cylinder rather than packed valves, noting that the packing material will absorb heavy components and aspirate them into flows of other raw materials.

Liquids are added to the recipient cylinder from syringes through a needle port on the valve. Before a syringe is filled with the first component, a vacuum is drawn on the syringe to clean out air or residue from previous contents. (To minimize equipment costs, one or two sample cylinders or syringes are used to transfer many different components into the blend; the vacuum cleaning method minimizes cross-contamination between components.) The empty syringe is placed on a tabletop balance, and the balance is tared to read zero. The syringe is then used to draw the desired amount of liquid component from the supply. The syringe and its contents are weighed again to determine the mass of component drawn from the supply. The liquid is injected into the recipient cylinder, and the emptied syringe is weighed once more to measure any residual liquid. The mass added to the blend is then computed by subtracting the mass of the emptied syringe from the mass of the full syringe.

Similar steps are used with transfer cylinders for gaseous components. Different sizes of cylinders are used, depending on the amount of gas required. As with the syringes, a vacuum is drawn on the transfer cylinder before each use to remove the previous contents, and the cylinder is weighed before new material is added. When the transfer cylinder is connected to the raw gas supply, steps must be taken to purge air from the connection. This can be done either by briefly “popping” the supply connection open to flush it with raw material, or by drawing vacuum on the connector after the transfer cylinder is connected. The transfer cylinder is then filled with raw material, and weighed on a balance to determine the mass of component drawn from the supply. After the gas transfer cylinder and transfer assembly are connected to the recipient blend cylinder, a vacuum line is connected to the transfer assembly to remove air or potential contaminants from the assembly. The vacuum line is closed, and the diaphragm valve and transfer cylinder valve are opened, allowing the vacuum in the recipient cylinder to draw in the product. Finally, all valves are closed, and the transfer cylinder is removed and weighed again to quantify the gas left behind in the cylinder.

Components are normally added in order of increasing vapor pressure (usually, corresponding to decreasing carbon number) to preserve the vacuum in the recipient cylinder during the blend process. One preparation facility adds components in order of increasing mole fraction, if the requested blend is rich in heavy hydrocarbons. After the last component is added, the cylinder is placed horizontally on a rolling device to thoroughly mix the contents.

Both facilities were asked about their procedures for avoiding phase change of gases to liquids during the blending process. One site employs a pressure gauge to check for condensed liquids in the transfer assembly. After a fill, the valves to the recipient cylinder and transfer cylinder are closed, and the vacuum line is used to remove any residual material in the transfer assembly. If liquids have condensed in the assembly, they will cause a noticeable fluctuation in the gauge reading as they revaporize under vacuum and leave the assembly. Since condensation represents a loss of part of the raw material, the blending process is stopped and the unfinished batch is discarded. The other facility uses a heat gun to vaporize any condensed liquids that may have been left in the transfer assembly, and then withdraws the vapor from the assembly, under the assumption that the condensed hydrocarbons represent a small error.

Information from the surveys was used to select suppliers of gas blends for hydrocarbon dew point experiments funded by GRI. Some survey questions were used to glean information on special capabilities related to the dew point gas blends. The gas compositions chosen for these tests simulated production and transmission-quality gases from 1,000 to 1,500 Btu per standard cubic foot (Btu/scf), and contain specific amounts of nitrogen, carbon dioxide, hexane and heavier hydrocarbons. Participants were asked to describe any special procedures used to prepare gases with these components. One respondent stated that all gravimetric filling processes, production, analysis and quality assurance/quality control (QA/QC) steps are documented in procedures and used for all reference gas preparations, regardless of the components. Three of the respondents had specific approaches to preparing blends with these components.

- One company always adds hexane and heavier hydrocarbons first, while the cylinder is under vacuum. Heat is used as necessary to ensure complete addition of materials. All raw products are analyzed for N₂, CO₂, O₂, and other diluents or impurities.
- One company uses micro-weighing techniques to accurately weigh small quantities of liquid components (heavy hydrocarbons) that are transferred via syringes. Fittings on transfer syringes are used to prevent evaporation of the more volatile components. The syringe is weighed before and after filling, and again after the liquid is dispensed. A notable practice is the use of a series of diluted pre-mixtures in methane where components are required at low concentrations.

- Another company uses computer programs to calculate quantities for addition as necessary. Typically, a vendor supplies all components through C₄ and inert diluents, while the remaining hydrocarbons are calculated and added from in-house stocks.

The companies were also asked the highest temperature and pressure at which reference gases can be prepared. This requirement is unique to the hydrocarbon dew point application. Gases that are used to calibrate chromatographs need not be delivered at high pressures, and the maximum preparation pressure cited by most companies is more than adequate for GC calibration. Rich gas blends, however, tend to have high dew points and must be prepared at high pressures and temperatures, but many companies do not routinely prepare blends above ambient temperature. Responses from the surveys follow.

- “Normally, up to 2,000 psia at 70°F.”
- “Standards are heated to a maximum of 125°F. Standards have been prepared at pressures of 2,000 psig, which is above the cricondentherm.”
- “In those cases where the cylinder pressure is not limited by the composition, a maximum of 2,900 psia can be achieved (the maximum rating of many sampling systems).”
- “Ambient temperature and 2,000 psig, but the upper pressure limit may be lowered because of hydrocarbon dew point considerations.”

4.5 Steps Taken to Avoid Condensation and Blend Distortion

During a site visit, it was noted that one facility uses commercial needle valves at each end of their gas transfer cylinders. Joule-Thomson cooling can occur as gas flows within needle valves and other narrow passages, and this mechanism is suspected to be a common cause of condensation and mixture distortion when gases are sampled. Although the facility in question can prepare rich blends well above heating values of 1200 Btu/scf, it does not consider the use of needle valves to be a significant source of phase change and condensation during raw material transfers.

As part of the survey, companies were asked what precautions are taken to ensure that Joule-Thomson cooling through the control valves does not cause phase change of the raw materials or distortion of prepared blends. Two of the five facilities take precautions to avoid condensation during the blending process. Heat tracing of lines and valves is used as appropriate, and transfers are performed at a slow rate, so that cooling is limited, “as detectable by touch,” according to one response. Another facility applies heat to the transfer apparatus as necessary, but states “phase changes are not a factor in our gravimetric blending procedure.”

- ⇒ A recommended practice is to create blends from pure components where practical. If phase change occurs during the addition of a pure component, a gravimetric analysis of the amount added to the recipient cylinder will still be valid. The composition of a blended raw material will be distorted by phase change, and in this case, gravimetric data on the amount added will not be useful. Only blends that are not susceptible to phase change (such as a C₆₊ liquid blend) should be used as raw materials in creating reference gases.

4.6 Use of Balances

The mass of each component added to a blend is almost always measured using balances. Tabletop balances are used to measure small amounts of material added by transfer cylinder or syringe. Almost always, the transfer container is placed on the balance, the balance is tared, then the component is added to the transfer container, and the full container is weighed again to confirm the added mass of raw material. For large amounts of components (typically methane) that are beyond the range of tabletop

balances, a large floor balance is used. The recipient cylinder is moved onto the balance, and the balance is tared, then the mass of added methane is measured during the fill.

Two practices observed at the test facilities are taken from ISO guidelines on gas blend preparation, and are listed here as recommended practices:

- ⇒ Enclosures around tabletop balances are recommended to minimize fluctuations in reading caused by drafts. Balances used to measure small amounts of material are often sensitive to moving air, making these enclosures necessary to avoid introducing bias errors.
- ⇒ Markings or “targets” on floor balances should be used to ensure that cylinders are weighed in the same location each time. Depending on the mechanism, a cylinder may give different readings at different positions on the balance, resulting in seemingly random measurement errors.

4.6.1 Traceability and Calibration of Balances

Traceability of measurements to a metrological standard gives preparation companies and calibration gas users confidence in the accuracy of blend composition by helping to eliminate measurement bias. For example, reduced uncertainty in a calibration gas composition leads to reduced uncertainty in GC analyses of gas streams, reduced uncertainties in calculated gas properties, and a potential reduction in unaccounted-for gas and fiscal errors for companies that buy, sell and transport natural gas.

Four of the five companies surveyed calibrate their balances using masses (“weights”) that are traceable to the U.S. National Institute of Standards and Technology (NIST), the Institute for Metrology and Technology in the Netherlands (NMI), or an appropriate national organization. These four companies follow written procedures or quality assurance programs to achieve consistency in calibrations. One company stated that they send their balances to the appropriate organization for calibration. No mention was made of any steps taken to ensure that the transportation of balances from the calibration site to the company does not alter the calibration, however. During visits to two of the gas preparation sites, both sites reported that their balances are monitored every morning using at least two masses traceable to national or international standards. One site has a specific procedure for checking balances that fall out of tolerance and removing them from service. Some recommended practices observed during the site visits:

- ⇒ One site uses quality control charts to track the behavior of their balances from day to day. Control charts are used in industrial and scientific applications to keep records of equipment performance, to identify trends in performance, and to determine imminent problems with the balances before they become significant.
- ⇒ Both sites have a third party inspect balances and calibration equipment on a regular basis. The work by the outside party may take the form of an independent calibration of balances in place, and verification that the traceable masses used to calibrate the balances are accurate.

4.7 Analytical Verification of Blend Compositions by Gas Chromatography

As mentioned at the beginning of this chapter, four of the five companies surveyed prepare their reference gas blends using gravimetric measurements of each component as it is added. The accepted tool to verify the composition of reference gas blends is gas chromatography. Laboratories normally use dedicated GCs to confirm that the distribution of components are as calculated from gravimetric measurements. If the analytical composition disagrees with the composition derived from gravimetric data, the laboratory may use the analytical data to adjust the final certified blend, or reject the blend, depending on the size of the disagreement and laboratory procedure. Details of these approaches are discussed in Chapter 5.

Laboratory GCs are typically used to analyze all components of natural gas blends. Within a GC, a sample of the gas flows through a long tube or column containing a material that briefly adsorbs and releases the different components of the gas. The length of time that each component adheres to the material in the column depends on properties of the component, properties of the material, the temperature of the column, and the gas flow rate. The components of the gas sample then elute from the column at different times, so that the column effectively separates the gas sample into methane, ethane, propane, and other components. A detector responds to the passage of each component from the column, with larger amounts producing larger responses. An integrated time trace of the detector response can then be used to quantify the amount of each component. Because of the various properties of natural gas components, multiple column types are needed to fully analyze a gas blend. Methane through pentane may be measured by one type of column, hexane and heavier hydrocarbons measured by a second type of column, and diluents measured by a third.

Two respondents discussed precautions taken while verifying the final blend compositions via GC analysis. In one case, prior to analysis, phase diagrams of the final blend are constructed, and isenthalpic flash calculations are performed to determine whether the mixtures are likely to condense during sampling or transfer. Those mixtures subject to phase change are transferred through heated lines and heated pressure reduction equipment. Multiple pressure-reduction stages are also used to minimize the Joule-Thomson cooling effect.

4.7.1 Traceability and Calibration of Gas Chromatographs

Ideally, a gas chromatograph used in checking reference gas compositions would be calibrated with a gas blend whose composition is verified by other means. Although GC calibration gas blends should be gravimetrically prepared, the gravimetric composition must often be verified by GC analysis. A laboratory that gravimetrically prepares a calibration gas, uses the gas to calibrate its own GCs, and then verifies other calibration gases with the GC, risks the possibility of undetected biases in its preparation process. Any biases in the preparation process would create similar biases in chromatograph response factors.

Just as balances used to weigh components can be calibrated using masses traceable to a national standards organization, chromatographs used to validate the gravimetric compositions can also be calibrated against national standards. Two of the companies surveyed calibrate their GCs using reference gases that are traceable to NIST or an equivalent organization. NIST prepares its own reference gases, and can supply gravimetric calibration standards containing methane, ethane, propane and diluents. Traceable reference gases with heavier hydrocarbons are not available from NIST, so that direct traceability of a GC calibration in butane and heavier hydrocarbons is not currently possible. NIST does coordinate a Traceable Reference Materials Program, in which commercial vendors produce certified gas standard blends that are distributed by NIST. However, the certified compositions are derived statistically from multiple GC analyses, rather than gravimetric data. The program was established in 1990 to provide users of GCs that analyze vehicle emissions with a means to accurately analyze pollutants and exhaust gases for the EPA. Hydrocarbon gas blends of interest to the natural gas community can also be prepared under this program, so that indirect traceability of GC calibrations in butane and heavier hydrocarbons may be possible.

One laboratory that participated in this study does gravimetrically prepare its own calibration standards. The facility recognizes the potential for bias in this procedure. In order to reduce the risk, diluents and hydrocarbons from methane through butane are obtained from different suppliers. The potential for bias still exists in GC calibration factors for pentanes and heavier hydrocarbons.

Several laboratories apply quality control methods similar to those used for balances to their GCs. One company calibrates its GC immediately before every sample analysis as a method of preventing

instrument drift. Another lab compares consecutive GC calibrations to quantify analytical repeatability, and compares calibrations on different days to quantify analytical reproducibility.

- ⇒ One gas preparation company calibrates their chromatographs using seven different gases, each with a different concentration of methane, ethane, and other components. This seven-point calibration method is based on ISO procedures, and can identify nonlinearities in response factors. Multiple point calibrations, as described in ISO 6143 (Reference 13), are a recommended practice.

4.8 System Balances

The term “system balance” usually refers to a method of accounting for lost materials, or to a method used to confirm the amounts added to the final blend. Imbalances can signal loss of raw material through condensation or leaks, and can indicate problems in the final blend. Respondents were asked what methods are used to account for “lost mass” or adsorption of materials, and how are these included in the uncertainty analysis of the certified composition.

Of the five companies surveyed, only three appear to perform a specific system balance during gas preparation. Of these three, one laboratory calculates lost mass based on the residuals left in the transfer container and transfer assembly. Residual amounts of gases in transfer cylinders are measured after each component is added to the blend. From this measurement, the known volume of the cylinder and the calculated volume of the transfer assembly, the theoretical residual left in the transfer assembly is computed. These two amounts are subtracted from the original mass of material in the transfer cylinder to arrive at the mass added to the recipient cylinder. This level of detail is considered necessary by the facility to achieve small uncertainties in gravimetric blends.

The more common system balance method, used by the other two companies, is the comparison of gravimetric and analytic gas compositions. Here, the GC analysis verifies the accuracy of gravimetric values, and does not quantify lost mass. Differences between the amounts computed from balance measurements and from chromatograms can be used to detect impurities in raw materials, errors in gravimetric measurements, or other system imbalances. One company includes an uncertainty analysis in both their gravimetric and analytic results. The other uses “normalization” to detect imbalances, although no details were given on this approach. Their certified compositions are based exclusively on multiple GC analyses of each blend, with no gravimetric data involved.

- ⇒ The use of quality control charts to assess product stability, similar to the use of control charts for tracking the performance of balances and traceable equipment, is a recommended practice to identify potential problems in the blending process.

Of the two facilities that do not compute lost mass, one responded with the following comments.

- “Lost mass is a bias that cannot be included in a weighing uncertainty analysis. Biases should always be corrected, not included as an uncertainty. Minimizing these biases can be achieved through the use of micro-weighing techniques.... Adsorption of materials onto the surface of cylinders is extremely difficult to model.... A more pragmatic approach is to conduct stability studies over extended periods to assess product stability.”

5.0 Uncertainties in Reference Gas Compositions

As part of the survey of gas preparation companies discussed in Chapters 3 and 4, the participants were asked to describe their methods of determining uncertainties in certified compositions and provide typical uncertainties for their gas blends. Specific requests included the confidence levels of computed uncertainties, the sources of uncertainty data, and example certificates of analysis. The results are presented in this chapter, but have been blinded and are not identified by company.

Of the five companies that participated in this study, three perform statistical analyses of gravimetric measurements based on balance uncertainties, calibration mass uncertainties, raw product impurities, and related quantities. A fourth also performs gravimetric statistical analyses, but the details of their methods were not made available. The fifth does not use gravimetric methods to prepare its blends, but uses repeated GC analyses to derive uncertainties in composition.

Approaches to obtaining certified compositions from the data also vary. Two companies use the gravimetric compositions directly as certified values for the blends. Uncertainties in the certified values are taken from statistical analyses of the gravimetric measurements, and analytical compositions from GC analyses are used only to verify the gravimetric values. A third facility uses the opposite approach: it reports the analytical values in the certified composition, and verifies them using the gravimetric data. Uncertainties in the analytic GC composition from this company are based on GC response factors and analyses of traceable reference gases. A fourth facility uses a hybrid approach, averaging gravimetric and analytic values if the GC analysis shows limited deviation from the gravimetric numbers. The adjusted values then appear in the certificate of analysis, with uncertainties based on both gravimetric and analytical data. The fifth company does not use gravimetric data in any way, but instead applies a GC analysis for the certified composition, and employs statistical analyses of repeated GC measurements and measurements of traceable standards to define uncertainties in the composition.

For users of GCs to assess the potential uncertainties in their analyses, the certified compositions of GC calibration gases must include uncertainties in each component. Respondents were asked to provide example certificates for review. The information available to users in the analysis certificates was found to vary significantly. Two of the five examples included compositions and uncertainties in mole percent, while another example included compositions in mole percent and composition uncertainties in percent of value. The other two example certificates did not list any uncertainties in compositions, but provided enough information in their survey responses for uncertainties to be determined.

Table 2 compares the uncertainties in the example compositions provided by each company. The uncertainties are listed as percent relative values, with statistical confidence levels appearing at the top of the table. For instance, in Example C, the concentration of nitrogen is 2.466 mole % ± 0.61 % relative, or 2.466 mole % ± 0.015 mole %, at the 95% confidence level. The participant that provided the data in Example B reported 1% relative uncertainties in each component, but was unable to provide the information needed to determine the confidence level of the uncertainties. The participant that provided the data in Example E reported uncertainties at the 99.5%, or 3-sigma, confidence level.

Table 2. Comparison of uncertainties in certified compositions from various reference gas preparation sites.

Component	Example A		Example B		Unknown		Example C		Example D		Example E	
	Amount (mol %)	U ₉₅ (% relative)	Amount (mol %)	conf. level (% relative)	Amount (mol %)	U ₉₅ (% relative)	Amount (mol %)	U ₉₅ (% relative)	Amount (mol %)	U ₉₅ (% relative)	Amount (mol %)	U _{99.5} (% relative)
nitrogen	1.27	0.79%	1.01	1%	2.466	0.61%	1.247	1%	0.253	0.05%		
CO ₂	0.792	0.76%	2.00	1%	0.985	0.71%	1.244	1%	0.248	0.34%		
methane	95.12	0.07%	balance		90.654	0.31%	92.623	1%	91.026	0.25%		
ethane	2.45	0.29%	6.06	1%	4.057	0.71%	2.977	1%	5.845	0.21%		
propane	0.253	0.79%	3.99	1%	1.008	0.79%	0.547	1%	1.504	0.06%		
isobutane	0.041	2.44%	0.506	1%	0.1984	0.71%	0.273	1%	0.402	0.02%		
n-butane	0.041	2.44%	0.495	1%	0.1970	0.81%	0.275	1%	0.422	0.15%		
neopentane					0.1113	1.62%						
isopentane	0.01	10.00%	0.252	1%	0.1082	1.48%	0.273	1%	0.122	0.42%		
n-pentane			0.252	1%	0.1078	1.48%	0.275	1%	0.076	0.68%		
n-hexane	0.026	7.69%	0.0504	1%	0.1032	1.94%	0.266	1%	0.102	0.40%		
n-heptane			0.0253	1%								
n-octane			0.0248	1%								
Total	100.003				99.996		100.000		100.000			

Methods used to determine compositions and uncertainties:

Gravimetric analysis?	no	yes	used as check	if scale 1% accurate	primary
GC analysis?	yes	at option of customer	primary	if scale not 1% accurate	used as check

System balance or methods used to account for lost mass:

Multiple GC analyses of each blend	Written procedures	Minimized through micro-weighing	GC analysis	Residuals in transfer container
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6.0 Conclusions

Five companies that prepare natural gas blends as reference gases or chromatography calibration standards participated in a survey of the “state of the art” of gas preparation practices. The participants provided information on their methods of preparing gas blends; the equipment used to store, transfer and blend gases; the purity of raw materials; and methods of computing uncertainties in the final certified gas blends. From this information, typical composition uncertainties were determined, potential sources of error or increased uncertainty were identified, and “best practices” were suggested to the API MPMS Chapter 14.1 Working Group as ways to reduce error in gas blends.

The examples of certified gases in Chapter 5 demonstrate that composition uncertainties of 1% of value or less, at the 95% confidence level (U_{95}), are routinely attainable in hydrocarbon components from methane through isobutane and normal butane. U_{95} uncertainties of less than 1% in the heavier hydrocarbons are achievable by some companies, particularly those with high-precision balances. Those participants that are able to achieve this low level of uncertainty use gravimetric analyses in their work, either to determine the blend composition directly or to verify certified compositions determined by GC analysis. The research by Cowper (Reference 5), which indicated that uncertainties in computed dew point of 0.5°F may be possible, assumed U_{95} uncertainties in gas composition of 1.4% relative in n-pentane and 2.6% relative in n-hexane. Most of the calibration gases listed in Table 2 would make it possible to compute dew points to this level of uncertainty, if the heavier hydrocarbons could be measured to the parts-per-million level suggested by Cowper.

During the review of gas blending methods, some techniques and equipment with the potential to cause errors in blending and possible inaccuracies in certified compositions were observed.

- At least two preparation companies reported that they employ stainless steel needle valves in raw material transfers. Joule-Thomson cooling through needle valves, and similar temperature changes in transfer equipment, can cause heavy hydrocarbons to condense or vaporize and pose problems during component delivery. Condensation of pure components could lower the amount reaching the final cylinder if gravimetric methods are not properly used, or the condensed material could conceivably contaminate other raw materials passing through the same equipment.
- Some companies store large amounts of gaseous raw materials outside or in areas that are not climate-controlled. For volatile gases (such as butane or pentane) that could change phase when stored outside under the right conditions, outside storage may lead to problems similar to those potentially caused by needle valves.
- To minimize equipment costs, one or two sample cylinders or syringes are commonly used to transfer many different pure components into the blend. A vacuum method is used to clean the syringe or cylinder after each component is transferred, but care must be taken that this step effectively removes each component before the next is added, or the potential will exist for contamination of other raw materials handled by the same container.
- Mixing old and new batches of raw materials is not an accepted practice. In the event that different batches are combined in a raw material reservoir, the new purity of the source material must be determined, and uncertainties in the composition of the raw material and final certified blends can be expected to increase.
- At least one of the participating companies states that they obtain nearly all their stock material from a single supplier. This practice may lead to consistent impurities in raw materials that, if not detected, may produce biases in the certified gas blends. Depending on how the mixtures are certified, the biases may or may not be detected by the blender, but

would be noticeable by laboratories or facilities that rely on other suppliers of calibration gases.

- GC calibration gases are gravimetrically prepared, but the composition of gravimetrically prepared gas blends must be verified by GC analysis. A laboratory that gravimetrically prepares a calibration gas, uses the gas to calibrate its own GCs, and then verifies other calibration gases with the GC risks the possibility of undetected biases in its preparation process. Any biases in the preparation process would create similar biases in chromatograph response factors. Laboratories that prepare their own calibration gases may benefit from participating in round-robin programs to compare their analyses to those of other labs and identify such biases.
- One company states that they send their balances offsite for traceable calibration. The process of transporting the balances back to the company may alter the calibration if the balance is not properly packaged and delivered. *In situ* calibration of the balance is clearly preferred.

Several practices were identified that are suggested as “best practices” for calibration gas preparation. These are recommended as ways to limit contamination, remove measurement bias, or reduce overall uncertainty.

- ⇒ Materials in storage containers should be checked for compatibility with their intended contents before use.
- ⇒ Refrigeration should be used in storage areas to stabilize volatile raw materials.
- ⇒ Raw materials should be checked for impurities before use; gas chromatography is well suited for this task.
- ⇒ Uncertainties in the purity of raw materials analyzed after purchase, and impurities measured analytically by gas chromatography, should be used in generating certified compositions of final products.
- ⇒ When raw materials are transferred to storage cylinders, the cylinders should be placed in service and labeled according to Compressed Gas Association guidelines to guard against cross-contamination.
- ⇒ Blends should be created by adding pure components individually to the mixture, or by adding liquid blends that are not susceptible to phase change (such as C₆₊ blends). Blends that can change composition when heavier components condense out should be avoided.
- ⇒ Enclosures around tabletop balances are recommended to minimize fluctuations in readings caused by drafts.
- ⇒ Markings or “targets” on balances should be used to ensure that cylinders and containers are weighed in the same location each time. Depending on the mechanism, a cylinder may give different readings at different positions on the same balance.
- ⇒ Multiple point calibrations of gas chromatographs, as described in ISO standard 6143, are a recommended practice.
- ⇒ Quality control charts are recommended to track the behavior of balances over time, and to determine imminent problems with the balances before they become significant. The use of quality control charts to assess product stability is also a recommended practice, as it can identify other sources of error in the blending process.

⇒ Third party checks of the calibration equipment, such as independent balance calibrations and verification of traceable masses, should be performed on a regular basis.

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7.0 References

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Appendix

Surveys of Reference Gas Preparation Companies

This Appendix presents the two surveys sent to all research participants. Identical initial surveys were sent to all gas preparation companies. Follow-up surveys contained a core set of common questions, plus individual questions unique to each participant. These company-specific questions served to clarify responses in the first survey, or to gather information similar to that provided by other companies and place all participants on an equal footing where possible. Only the core questions appear in the follow-up surveys here, in order to keep survey results blinded. In the interest of conserving space, blanks in which participants recorded their survey answers have been removed, leaving only the survey instructions and questions.

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Survey of Companies who Prepare Chromatographic Calibration or Reference Gas Standards

Darin L. George

Southwest Research Institute

May 2002

As part of our continuing work to support the Gas Research Institute (GRI)/American Petroleum Institute (API) Ch. 14.1 Natural Gas Sampling Research Project Working Group (WG), Southwest Research Institute (SwRI) is conducting a survey of companies that prepare chromatographic calibration or reference gas standards for the natural gas industry. The purpose of the survey is to document the methods used to prepare the chromatographic calibration or reference gas standards, and to establish an overall uncertainty for the resulting gas compositions. As part of the project, SwRI will visit a number of the companies to observe their procedures and equipment. In addition, SwRI will order chromatographic calibration or reference gas from several companies. The chromatographic calibration or reference gas standards will be used (1) to study uncertainties in gas chromatograph (GC) calibrations, and (2) in tests to collect hydrocarbon dew point data for a natural gas database. The API 14.1 WG will use this information for future revisions of API gas sampling standards.

The API Ch. 14.1 WG would like to thank you for agreeing to support the work of this standards group. Please provide the following information about your facility, procedures, and records. Be assured that the information you provide will not be associated with your company, but your participation will be acknowledged.

Your name:	
Your company:	
Your address:	
Your e-mail:	

1. Equipment

What types of **containers** are used to **store raw materials and stock gases**?

What are the construction materials of these containers?

What type of **pressure and flow regulation devices** are used for the dispensing of raw materials?

What are the construction materials of these pressure and flow regulation devices?

What types of **containers** are used to **transfer** raw materials and stock gases to the final product containers?

What are the construction materials of these transfer containers?

Questions about the containers for the final product can be found in Section 4.

2. Regulatory Compliance

With what regulatory agencies do the equipment and products listed in Section 1 comply?

How is compliance accomplished?

What routine maintenance, if any, is done on the equipment listed in section 1?

3. Source materials

What is the purity of the raw materials used to prepare reference gases? How are these purities determined?

How are changes in the purity of raw materials over time accounted for?

What criteria determine when raw materials are replaced?

If raw materials are refreshed by adding new lots of materials to old lots of materials, how are the possible changes in purities determined?

4. Reference gas preparation

What methods and equipment are used to transfer raw materials to the mixing location?

Describe the containers that hold the final product.

What are the construction materials of these final product containers?

How are the required amounts of each component determined?

What equipment is used to measure the required amounts of each component?

Is any of this equipment traceable to a national organization or standard? If so, which organizations and standards?

What equipment used is not traceable?

How is the equipment, traceable and non-traceable, calibrated?

Are the references used to calibrate the equipment traceable to a national organization or standard? If so, which organizations and standards?

What are the tolerances for all of the equipment and references?

What are the linearity and repeatability limits of the traceable and non-traceable equipment and references?

What methods, if any, are used to ensure a “system balance” and minimize unaccounted-for raw materials?

What standard methods, if any, are applied in the preparation process?

Are written procedures used during the preparation process? Are they available for review?

Is the work of personnel directly observed by others during the preparation process or reviewed after completion?

5. Uncertainties in reference gas composition

How are the uncertainties in the final product composition determined?

Are the compositions verified using separate instrumentation? If so, what instrumentation?

How are these instruments calibrated and at what frequency?

What are the linearity and repeatability limits of the instruments?

What is the source, composition, traceability, and tolerance limits of the reference materials used to calibrate the instruments?

What other methods are used to verify the final product composition?

How are the certified component concentrations determined?

Please provide an example of a final composition certificate.

6. Record keeping

How long are calibration certificates and records for traceable and non-traceable equipment kept?

How long are records of product compositions and uncertainties kept?

How are these records used?

What, if any, quality control (QC) programs are used at your facility?

How are personnel trained in QC procedures?

How often, and by what process are duplicate standards prepared and compared to each other (to monitor preparation repeatability)?

**Survey of Companies who Prepare Chromatographic Calibration or
Reference Gas Standards:
Follow-up Questions**

**Darin L. George
Southwest Research Institute
July 2002**

The GRI/API Ch. 14.1 Natural Gas Sampling Research Project Working Group would like to thank you for participating in the survey on natural gas preparation. I would also like to thank you for your input and your enthusiasm in helping with this study.

At the API Ch. 14.1 meeting on June 25, I presented the survey findings to the Working Group. We discussed the methods companies used to prepare mixtures, their calculation of uncertainties, and the ways in which companies certify gas compositions. The information was not associated with individual companies that provided it, to keep proprietary information confidential.

After the presentation, the Working Group agreed on several additional questions to ask all participants. They also listed specific questions to ask individual companies, so that all respondents can be placed on an equal footing in the final report. I have created a short questionnaire with the extra questions for your company. I have also attached your first questionnaire to this e-mail for reference. Please review the questions in this follow-up and answer them to the best of your ability. Please return all follow-up questionnaires by July 15, 2002.

On behalf of the Working Group and myself, thank you again for your help.

Your name:	
Your company:	
Your address:	
Your e-mail:	

1. Equipment

What steps are taken to clean and prepare **containers** for **raw materials and stock gases**? What cleaning agents are used?

What steps are taken to clean and prepare **pressure and flow regulation devices**? What cleaning agents are used?

What steps are taken to clean and prepare **transfer containers**? What cleaning agents are used?

What liquid or gas is used to purge the equipment?

What materials are used in the seals of the pressure and flow regulators?

What precautions are taken to ensure that Joule-Thomson cooling through the valves does not cause phase change of the raw materials?

2. Source materials

Please give quantitative values of the purity of the raw materials used to prepare reference gases (99%, 99.9%, etc.).

What methods are used to measure impurities in raw materials?

3. Reference gas preparation

Describe any special procedures used at your facility to prepare gases with specified amounts of nitrogen, CO₂, hexane or heavier hydrocarbons.

What are the highest pressure and temperature at which reference gases can be prepared?

4. Uncertainties in reference gas composition

What are the statistical confidence limits on uncertainties in the certified product composition?

Please provide an example uncertainty analysis of the certified composition.

Is a GC/gravimetric analysis ever used to determine the certified product composition?

What methods are used to account for lost mass or adsorption of materials? How are these included in the uncertainty analysis of the certified composition?