Obtaining Natural Gas Samples for Analysis by Gas Chromatography

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INTRODUCTION

This 2005 revision of GPA (Gas Processors Association) Publication 2166 contains major changes from the 1986 version. The incorporated changes are the result of a cooperative sampling program carried out by the API (American Petroleum Institute) workgroup on Natural Gas Sampling. Data from the API project combined with data from a GPA project published in 1985 provide the impetus for this latest revision.

A "definitions" section has been added to help the reader understand the terms used throughout this document. Words in **bold type** are defined in the "definitions" section. First uses of TLAs (Three Letter Acronyms) are followed by an explanation in parentheses. Subsequent use of the TLA is not followed by a parenthetical explanation.

This publication includes detailed sampling procedures for each of 8 test methods:

1. Purging - Fill & Empty Method
2. Purging - Controlled Rate Method
3. Evacuated Container Method
4. Reduced Pressure Method
5. Helium "Pop" Method
6. Glycol or Water Displacement Method
7. **Floating Piston Cylinder** Method
8. Portable and On-Line Gas Chromatographs

Not all methods are appropriate for all sampling conditions. Appropriate sampling conditions for each method are discussed in this standard.

It is important to have a thorough knowledge of the phase behavior of the product to be sampled and of the **Joule-Thomson Effect**. Discussion of the **Phase Diagram** and the **Joule-Thomson Effect** can be found in API Chapter 14.1.

The sampling methods listed in this document require that the sampling components are clean and free of contaminants. It may be necessary to clean sample cylinders and sampling system components between uses. Appendix A of this document discusses cleaning of sample system components.

The data from the API 14.1 sampling project clearly demonstrated that misuse of the **Gas Sampling Separator** could distort the sample. The current revision of this GPA publication includes language to clarify the proper use of the separator. It discusses when the **Gas Sampling Separator** would be appropriate and explores the potential pitfalls associated with its misuse.

Obtaining Natural Gas Samples for Analysis by Gas Chromatography

1. Scope

1.1. The purpose of this publication is to recommend procedures for obtaining samples from flowing natural gas streams that represent the composition of the vapor phase portion of the system being analyzed. These representative samples are subsequently transported to a laboratory and analyzed for composition and/or trace contaminants or analyzed onsite by portable or on-line chromatographs.

1.2. The methods outlined in this publication are designed for sampling natural gas from systems that are at or above the **Hydrocarbon Dew Point** temperature. As the temperature of the flowing stream decreases or the pressure increases to impinge upon the **Hydrocarbon Dew Point**, it becomes increasingly difficult to obtain a representative sample of the flowing stream. This standard does not address accounting for the liquid hydrocarbon portion of two-phase systems.

1.3. The scope of this standard does not include composite gas sampling (samples taken in increments over relatively long time periods) systems. For information on composite sampling, the reader is referred to API 14.1 and ASTM D5287.

1.4. Due to a lack of supporting research data, the scope of this standard does not include sampling from vacuum sources.

2. Notes

2.1. General notes

2.1.1. Note 1

Streams containing hydrogen sulfide should be analyzed for hydrogen sulfide on site in the field.

2.1.2. Note 2

Moisture concentration cannot be determined from a sample container in a laboratory. Moisture determination in natural gas streams must be performed on site in the field or by moisture saturation calculations.

2.1.3. Note 3

All sampling system components between the sample point valve as defined in note 4 and the sample cylinder must be maintained above the **Hydrocarbon Dew Point** temperature. To date, the most accurate determination of **Hydrocarbon Dew Point** is the **Chilled Mirror Test**. By definition, the gas-phase portion of the product flowing in a two-phase system is at the **Hydrocarbon Dew Point** temperature. Calculated **Hydrocarbon Dew Points** are only as accurate as the accuracy of the calculation method and the detail and accuracy of the analysis.

Any component of the sampling system that separates unwanted liquids from the sample stream must be operated at flowing line temperature and pressure.

Downstream of the sample conditioning components of the sampling system, and where sample is to be purged, the downstream components must be maintained above the **Hydrocarbon Dew Point** temperature.

For purposes of this publication, the **Hydrocarbon Dew Point** temperature is considered one of the following: the flowing line temperature (at flowing line pressure), the value determined by a **Chilled Mirror Test** (at flowing line pressure), or 30 °F (17 °C) above the calculated **Hydrocarbon Dew Point** temperature. If the product flowing in the line is completely in the vapor phase the flowing line temperature is, of course, above the **Hydrocarbon Dew Point** temperature for the line pressure. But if any droplets of liquid have condensed in the flowing product stream, the flowing line temperature is equal to the **Hydrocarbon Dew Point** temperature for the line pressure. Therefore, if sample system components are maintained above flowing line temperature and at line pressure, the sampling system components will be above **Hydrocarbon Dew Point** temperature (unless the line is 100% liquid full).

2.1.4. Note 4

In Section 9, Sampling Procedures, the term "sample point valve" or "valve at sample point" refers to the valve at the outlet of the **Sample Probe**, regulator, membrane filter, **Gas Sampling Separator** or combination thereof.

2.1.5. Note 5

Pressure drops due to pressure regulators or flow control devices cause reduction in temperature due to the **Joule-Thomson Effect**. This can cause condensation in the sampling system. Therefore it may be necessary to heat regulators that are used to reduce the sample pressure.

For some sampling methods listed, flow control devices such as flow control plugs or valves should be located at the outlet of the **Sample Container**. These flow-controlling devices can cause cooling due to the **Joule-Thomson Effect**. To thermally isolate this cooling effect from the **Sample Container**, flow control devices should be placed at the outlet end of an **Extension Tube ("Pigtail")**, which is attached to the outlet of the sample cylinder.

Ambient cooling of the sample system can cause heavy hydrocarbons to condense out of the vapor phase. The presence of any condensation in the sample inlet system will cause the sample to be non-representative. Condensation must be avoided in the entire sample system from sample probe to sample cylinder outlet or chromatograph inlet.

2.2. Safety Notes

2.2.1. Safety Note 1

Hydrocarbon vapors are flammable and can be explosive. They can also replace breathing air. Refer to employer-provided safety bulletins. The sampling technician who uses any of these sampling procedures should be properly trained in the safe handling of natural gas and similar hydrocarbon materials.

2.2.2. Safety Note 2

Natural gas samples may contain components that cause health hazards other than flammability or replacing breathing air. Hydrogen Sulfide can be particularly dangerous. Prior to performing any sampling or analytical procedures, the analyst or sampler should be trained to be familiar with all possible hazardous contaminants, how to monitor for these contaminants and how to respond to various levels of these contaminants.

2.2.3. Safety Note 3

In some sampling situations and in most laboratory analysis, heating is required. Care should be taken to ensure that any heating device meets the requirements of all applicable codes.

Exceeding temperature limits could result in failure of components, fire and/or explosion. Electrical heating devices should be self-limiting to ensure that temperature limits are not exceeded. Electrical heating devices should have at least two methods of temperature control.

The Compressed Gas Association, Inc. states in CGA P-1-1991 that the temperature of compressed gas cylinder components should not exceed 125°F (51.7°C). If it is deemed necessary to heat the sample system components ensure that, according to manufacturer's specifications, all components in the sample system are rated for the higher temperature.

2.2.4. Safety Note 4

If the container is to be transported, it must meet local transportation regulatory specifications and be labeled according to the local transportation regulations. Containers should meet appropriate pressure and pressure relief requirements and should be safely secured in the transporting vehicle. Those who transport or ship **Sample Containers** must be trained in the current regulations. In the United States, refer to Hazardous Materials Regulations of the D.O.T. (CFR 49).

2.2.5. Safety Note 5

There is a theoretical possibility for auto-ignition of natural gas and air mixtures in gas sample cylinders if improperly filled (rapidly pressurized). Rapid opening valves should not be used in the sampling system. The only exception is that the outlet of the sample probe may have a ball valve.

Care should be taken to avoid rapidly opening the sample probe outlet valve to an open cylinder that is filled with air. The procedures outlined in this method are designed, through valve operation sequences, to prevent rapid filling of the cylinder.

2.2.6. Safety Note 6

Natural gas is often handled at high pressures. The sampling technician must be properly trained to work with compressed gasses. All sampling equipment should be rated equal to or higher than the highest expected pressure. Pressure reduction from pipeline to rated sample system pressure must be carried out with appropriately designed pressure regulators. Pressure relief devices should be used to protect from over pressure conditions.

3. List of Methods

3.1. A gas sample is transferred from the source into a **Sample Container** or gas chromatograph by one of the following methods:

3.1.1. Purging - Fill and Empty Method
3.1.2. Purging - Controlled Rate Method
3.1.3. Evacuated Container Method
3.1.4. Reduced Pressure Method
3.1.5. Helium "Pop" Method
3.1.6. Glycol or Water Displacement Method
3.1.7. Floating Piston Cylinder Method
3.1.8. Portable or On-Line Gas Chromatograph

3.2. The sampling system design and the sampling method selected will depend upon composition, pressure, temperature and **Hydrocarbon Dew Point** of the sample at source conditions.

4. General Information

4.1. The objective of the listed sampling procedures is to obtain a representative sample of the gas phase portion of the flowing stream under investigation. Any subsequent analysis of the sample, regardless of the accuracy of the analytical procedure, will not reflect the true composition of the flowing stream unless a representative sample is obtained. This method assumes all procedures begin with clean, leak-free **Sample Containers. Sample Containers** are discussed in section 7.1 and their preparation is discussed in Appendix A.

4.2. Entrained or free-flowing hydrocarbon liquids are generally collected and accounted for in a condensate recovery system. These liquids are not desired in the vapor phase portion of the accounting system. Other contaminants such as water, oil, glycol, amine, etc. are not desirable in the **Sample Container**. Since free-flowing liquids tend to flow along the bottom of the pipe or flow along the walls of the pipe, it is necessary to have a **Sample Probe** extending into the pipe. **Sample Probes** are discussed in section 7.5.

4.3. Flow disturbances may cause contaminants to form aerosols that can be ingested by the **Sample Probe**. These aerosols should be removed by filtration or separation in the sample system. Care should be taken not to alter the composition of the sample with these devices. Refer to section 7.3.1.

4.4. A **Gas Sampling Separator** may help to eliminate contaminants. **Gas Sampling Separators** are designed and tested to protect the analyzer from liquid contamination. They should not distort the composition of the sample. Proper use of **Gas Sampling Separator** is discussed in Appendix B.

4.5. Permanent or portable filters may be used. It is important to ensure that the filters are clean. Filters should only remove the unwanted contaminants and allow all components of interest to freely pass. Refer to section 7.3.1.

4.6. It is difficult to write sampling instructions explicit enough to cover all cases. Natural gas samples should be obtained under conditions that will not create condensation or vaporization in the sample system during the sampling process. This requires an understanding of the **Phase Diagram** for the stream to be sampled. Condensation due to the **Joule-Thomson Effect** or from ambient chilling can distort the sample. **Retrograde condensation** is difficult to predict without an understanding of the **Phase Diagram** for the product to be sampled. Discussion of the **Phase Diagram** and the **Joule-Thomson Effect** can be found in API Chapter 14.1.