# Obtaining Natural Gas Samples for Analysis by Gas Chromatography



Adopted as a Tentative Standard, 1966 Revised and Adopted as a Standard, 1968 Revised 1986, 2005

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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. <u>Scope</u>

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 ature 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 property 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 selflimiting 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 improperty 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.

4.7. Condensation may occur in the Sample Container during shipment. This condensation is not harmful provided that, prior to withdrawing any sample from the cylinder, the cylinder is heated sufficiently to ensure that all condensed liquids are returned to the vapor phase. The Sample Container must be heated prior to analysis. This will ensure complete vaporization of any liquid that has condensed after sample procurement. Refer to GPA 2261 for proper handling of gas samples in the laboratory.

#### 5. Hydrocarbon Dew Point

5.1. When the nature of the gas is completely unknown, the safest procedure is to assume that it is at the **Hydrocarbon Dew Point** temperature.

5.2. The initial determination of the system Hydrocarbon Dew Point temperature should be executed as described in API 14.1. Generally, this involves directly measuring the hydrocarbon (and water) dew point, calculating the dew point from a previous analysis or by collecting historical data. For any flowing gas stream that has both a vapor and liquid component, the Hydrocarbon Dew Point temperature of the vapor phase portion of the stream for line pressure is the temperature of the flowing gas stream.

5.3. The Hydrocarbon Dew Point must be considered when designing the sampling system and selecting the sample method.

5.4. The sampling procedure should be selected as specified in Section 6. This section discusses systems that are well above the **Hydrocarbon Dew Point** as well as systems that are at or near the **Hydrocarbon Dew Point**.

#### 6. Guide for the Selection of a Proper Sampling Procedure

See Table 1 for recommended equipment for each sampling procedure.

#### 6.1. Purging - Fill and Empty Method

This method can be used when the vapor phase portion of the flowing stream is at or above the Hydrocarbon Dew Point temperature. The temperature of the sample equipment downstream of the Sample Valve (Valve 1) must be maintained above the expected Hydrocarbon Dew Point (see Note 3, section 2.1.3) throughout the sampling process. It is necessary to use an Extension Tube ("Pigtail") with a flow control drilled plug or valve when using this method. It is important to adhere to the recommended number of purge cycles (See Table 3) to ensure that a representative sample is secured. Source pressure must be at least 15 psig (103 kPa guage).

#### 6.2. Purging-Controlled Rate Method

This method can be used only when the vapor phase portion of the flowing stream is above the Hydrocarbon Dew Point (see Note 3, section 2.1.3). Source pressure must be sufficient to produce critical flow conditions in flow plug (pressure of 15 psig (103 kPa guage) or greater and flow tube exhaust to the atmosphere). Extreme care should be used to prevent condensation during the sampling process. It is necessary to use an Extension Tube ("Pigtail") with a drilled plug when using this method. It is important to adhere to the recommended purge time (See Charts 1,2,3 and 4) to ensure that a representative sample is secured.

#### 6.3. Evacuated Container Method

This method can be used when the vapor phase portion of the flowing stream is at or above the Hydrocarbon Dew Point temperature. Users are cautioned that most valve styles are not vacuum-tight. Therefore, it is recommended that the cylinder be evacuated immediately prior to sample procurement. Source pressure must be at least 15 psig (103 kPa guage).

#### 6.4. Reduced Pressure Method

This method can be used when the vapor phase portion of the flowing stream is at or above the Hydrocarbon Dew Point temperature. There may be one or two objectives for reducing pressure: to reduce high pipeline pressures down to the pressure rating of the sampling equipment and/or to reduce the pressure enough to ensure that the sample is comfortably in the vapor phase. However, it is possible to reduce pressure and produce **Retrograde Condensation** in the process. This method is only applicable if the pressure reduction does not cross the phase boundary. See Section 8, Heating. See API 14.1 for discussion of the **Phase Diagram**. Source pressure must be at least 15 psig (103 kPa guage).

Safety Note: All sampling equipment should be rated for the highest expected sample pressure. Pressure reduction to sample system rated pressure must be accomplished with appropriately designed pressure regulators and pressure relief devices.