



Standard Guide for Collection of Multi-Media Field Emission and Discharge Data Associated with Glycol Dehydration Units¹

This standard is issued under the fixed designation E 1752; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Subsections 6.3.4 and 7.2.5 were corrected editorially in November 2000.

1. Scope

1.1 *Purpose*—This guide covers the proper collection of field emission and discharge data associated with glycol dehydration units used in the natural gas production, processing, transmission, storage, and distribution industries.

1.2 Background:

1.2.1 Increasing regulatory pressure has made emissions of benzene, toluene, ethylbenzene, and xylene isomers (collectively known as BTEX) and volatile organic compounds (VOCs) from the still vent of glycol dehydration units a major concern of the natural gas industry. The Clean Air Act Amendments (CAAA) of 1990 have been the impetus for air toxics regulations, and several states are regulating or are considering regulating emissions from glycol units (1).² Liquid and solid waste discharges are exempt from Subtitle C (hazardous waste) regulation under the Resource Conservation and Recovery Act (RCRA), but may be regulated in the future (2).

1.2.2 Measurement of the waste streams from dehydrators is important to determine which units may have emissions above levels of regulatory concern. Measurements of air emissions from glycol dehydration units have been made from a variety of sampling points using different sampling protocols and analytical techniques since no standard methods have been developed by the United States Environmental Protection Agency (USEPA) or state regulatory agencies. Standard sampling methods do not exist for the liquid and solid waste streams since they are exempt from RCRA Subtitle C. The lack of standard protocols has meant that variations of this approach can result in very different emissions measurements (3).

1.2.3 Providing guidance on the collection of field emission and discharge data will allow the natural gas industry to quantify emissions and apply appropriate controls to comply with regulations.

1.3 *Summary*—This guide has several parts and an annex. Section 1 is Scope. Section 2 is Terminology that has defini-

tions of terms commonly used with relation to glycol dehydration units in the natural gas industry. Section 3 is Significance and Use of this guide. Section 4 is a process description of glycol dehydration units. Section 5 is a discussion of the waste streams associated with glycol dehydrators. Section 6 presents the Approaches for Collecting Air Emission Data, while Sections 7 and 8 present the approaches for collecting liquid and solid waste discharge data, respectively. The annex includes a standard operating procedure (SOP) for the rich/lean glycol sampling method discussed in this guide.

1.4 The values stated in either inch-pound or SI units are to be regarded separately as the standard. The values given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Terminology

2.1 Definitions of Terms Specific to This Standard:

2.1.1 *BTEX*—the compounds benzene, toluene, ethylbenzene, and xylene isomers.

2.1.2 *Clean Air Act Amendments (CAAA)*—the 1990 federal amendments to the Clean Air Act. These amendments address nonattainment areas, hazardous air pollutants, permitting, and enforcement.

2.1.3 *condensate*—water or light hydrocarbons that have changed from a vapor to a condensed liquid state.

2.1.4 *contactor (or absorber)*—a vertical pressure vessel where gas and glycol are intermingled countercurrently to remove water vapor from the gas.

2.1.5 *dehydration*—removal of water vapor from natural gas. Maximum water content of the dehydrated gas is normally 7 lbs (3175 g) H₂O/MMSCF.

2.1.6 *flash tank*—a two- or three-phase separator that is used in the rich glycol stream to remove entrained gas and hydrocarbon liquid.

2.1.7 *gas absorption*—an operation in which a gas mixture is contacted with a liquid for the purposes of preferentially dissolving one or more components of the gas and to provide

¹ This guide is under the jurisdiction of ASTM Committee E50 on Environmental Assessment and is the direct responsibility of Subcommittee E50.05 on Wetland Ecosystems.

Current edition approved Oct. 10, 1995. Published December 1995.

² The boldface numbers in parentheses refer to the list of references at the end of the text.

a solution of these in the liquid.

2.1.8 *gas/glycol heat exchanger*—a shell-and-tube, pipe-in-pipe, or other type heat exchanger employed to cool the lean glycol with the gas leaving the contactor before the glycol enters the contactor.

2.1.9 *glycol*—a liquid desiccant used to absorb water vapor from the gas. Triethylene glycol is the most common glycol used in natural gas dehydration.

2.1.10 *lean glycol*—glycol that has been regenerated and is essentially free of water.

2.1.11 *rich glycol*—glycol that has absorbed water.

2.1.12 *reboiler*—the vessel where water is boiled out of the glycol.

2.1.13 *resource conservation and recovery act (RCRA)*—a federal regulatory measure for monitoring liquid and solid waste discharges. Subtitle C of the RCRA, as amended by the 1984 Hazardous and Solid Waste Amendments (HSWA) regulations, provides EPA the statutory authority to adopt a complex set of regulations for identification and management of hazardous waste from “cradle to grave,” that is, from the initial generation through the treatment, transportation, storage, and disposal of wastes.

2.1.14 *still column*—vertically mounted fractionation column on top of the reboiler.

3. Significance and Use

3.1 This guide on the proper collection of emission and discharge wastes from glycol dehydrators is applicable to any natural gas industry and supplier that operates glycol dehydration units and that needs to identify which glycol units may have emissions above regulatory levels.

3.2 The emission and discharge sampling methods discussed in this guide are not regulatory standards. Standard protocols have been developed by the Gas Research Institute (3) and other gas associations (4) and some state regulatory agencies such as the Louisiana Department of Environmental

Quality (LDEQ) (5) and the Texas Natural Resource Conservation Commission (TNRCC) (6) are accepting these data. This guide is **not** intended to instruct the user on how to perform the sampling using these protocols, but to make the user aware of certain practical considerations generally associated with sampling these waste streams.

4. Process Description

4.1 *Introduction*—Glycol dehydration units are commonly used in the natural gas industry to remove water from natural gas streams to prevent corrosion and hydrate formation in pipelines. Up to 40 000 glycol dehydration units may be in operation in the United States (7). TEG is commonly used as the dehydrant since it is more stable than other glycols (for example, ethylene glycol) at high temperatures. A brief description of a typical glycol dehydration unit is presented as follows.

4.2 Fig. 1 is a simplified flow diagram for a glycol dehydration unit. A glycol dehydration unit usually consists of an absorber, a flash tank, heat exchanger(s), filter(s), a glycol reboiler still, and associated pumping and piping equipment. The moist natural gas enters the bottom of the absorber, where it is contacted countercurrently with the cool, lean glycol that absorbs the water. The dry gas exits the top of the absorber.

4.3 The rich glycol (containing water) leaves the bottom of the absorber and often goes through a gas-driven balance pump to a flash tank, which is normally present only on larger units. The flash tank separates much of the natural gas captured under high pressure from the glycol; the flash gas may be used as a fuel source. After a series of heat exchangers and filters, the rich glycol enters the still and reboiler, where water is distilled and stripped from the glycol (some units inject a stripping gas to produce higher-purity glycol at normal reboiler temperatures). The lean glycol is pumped back to the top of the absorber from the surge tank.

4.4 Since some dehydrators may produce emissions that are

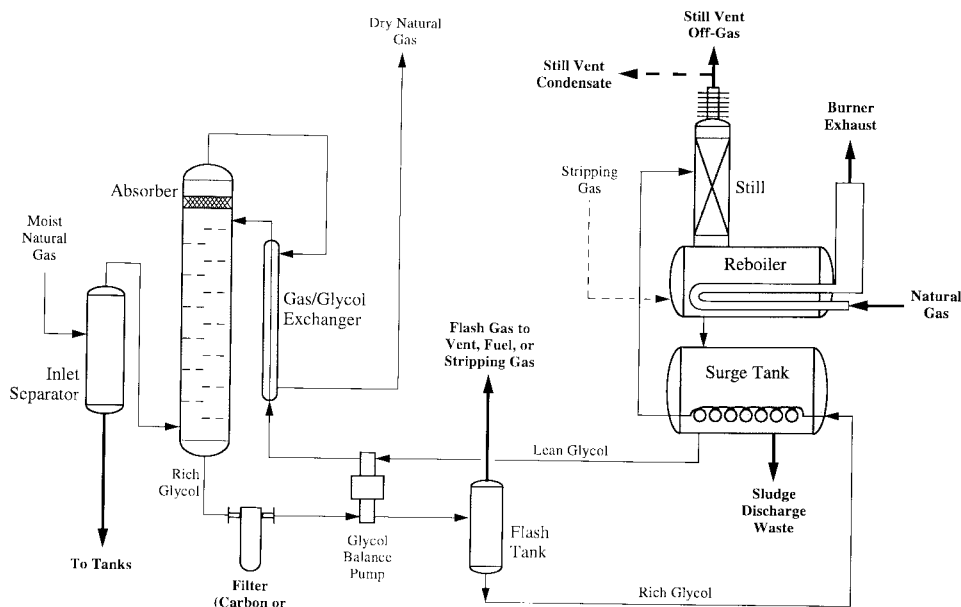


FIG. 1 Typical TEG Dehydrator Waste Streams

above the regulatory limits even with optimum operating conditions, several technologies have been developed to control emissions from glycol dehydrators. The two most common methods for controlling emissions are condensation and combustion (incineration).

4.4.1 Combustion of the vent stream is difficult, however, due to the possibility of condensation of hydrocarbons and water in the flare. Condensation of the flare results in smoking and incomplete combustion of the vapors. Operating costs for flares and incinerators are relatively high because no hydrocarbons are recovered for sale, and supplemental fuel is often required to sustain an adequate flame temperature (8).

4.4.2 Because of the difficulties associated with combustion, condensation has become the most widely used method of controlling emissions from glycol dehydrators. Condensers convert condensable components in the vapor phase to the liquid phase by reducing the temperature of the process stream. Condensers not only reduce emissions but also recover condensable hydrocarbon vapors that may increase production. The main types of condensers currently used by the gas industry are: air-cooled, glycol-cooled, water-cooled, and direct-contact quench condensers (8).

5. Waste Streams

5.1 *Introduction*— Possible waste streams generated by glycol units are shown in Fig. 1. Seven of the waste streams occur on many glycol units: still vent gas, burner flue gas, flash gas, water condensate, waste glycol, reclaimer waste, and spent filters. These waste streams and associated sampling considerations are presented as follows.

5.2 *Waste Streams and Sources:*

5.2.1 *Still Vent Gas*— During the absorption process, the glycol, that has a high affinity for aromatic compounds, removes BTEX and, to a lesser extent, other VOCs from the natural gas. (The BTEX compounds are usually present in the natural gas at levels of less than 1000 parts per million by volume, although concentrations can be higher in some cases.) Since the boiling points of BTEX range from 80 to 140°C, most of these compounds are not lost in the flash tank but are boiled from the glycol in the still. Although many of the lighter hydrocarbons may be removed from the glycol in the flash tank, some remain in the glycol and are also separated in the still. These separations in the still result in BTEX and other VOCs being present in the still vent gas, that is typically released to the atmosphere. This stream is the major source of air emissions.

5.2.2 *Burner Flue Gas*— Many glycol units use a gas-fired burner as the heat source for the reboiler. Since the natural gas combustion in these burners should be fairly complete, these burners should emit only minor quantities of VOCs. However, there will be some NO_x emissions as well as emissions of the combustion products of any gas contaminant.

5.2.3 *Flash Tank Vent Gas*—The flash tank removes a large fraction of the light gases absorbed by the glycol at high pressure by reducing the pressure of the rich glycol stream leaving the bottom of the absorber. The flash gas is often used as fuel, but may be vented as a waste stream at some units.

5.2.4 *Water and Hydrocarbon Condensate*—Many units also collect a water and hydrocarbon condensate from the

reboiler still vent gas. As the still vent gas passes through the stack above the distillation section of the column, some condensation may occur on the stack walls. The condensate may be collected through a drain leg off the stack and will likely be contaminated with hydrocarbon species. Still other units install condenser control technologies to recover additional liquid hydrocarbons from the still vent gas.

5.2.5 *Waste Glycol/Reclaimer Waste*—The glycol solution is occasionally replaced in units when it becomes fouled with contaminants such as heavy hydrocarbons, well-treating chemicals, corrosion products, degradation products, and salts. The contaminated glycol may be sent to a vacuum reclaimer for recovery.

5.2.6 *Spent Filters*— Filtration is used to remove low levels of contaminants from the solution and maintain solution quality. Sock filters are typically used in glycol units to remove particulates, while carbon filters are used to remove heavy hydrocarbons and surfactants from solution. These filters must be replaced on a regular basis.

5.3 *Sampling Considerations:*

5.3.1 *Still Vent Gas*— It is difficult to directly measure BTEX and VOC emissions by sampling the still vent stream. The stream temperature is in the range from 200 to 225°F (93.3 to 107.2°C) and may contain 90 + % water, as well as levels of organic compounds that may often be in the percent range. Problems associated with sampling and analyzing this stream include the following (3):

5.3.1.1 Measuring organic compounds in the presence of high levels of water or removing the water without biasing the organic compound measurements,

5.3.1.2 Collecting a representative, homogeneous sample from a low flow rate stream that may have condensing material, and

5.3.1.3 Accurately measuring the low, fluctuating flow rate of this stream.

5.3.2 *Burner Flue Gas*— The USEPA has characterized emissions from natural gas combustion and established factors for estimating these emissions (2). Therefore, sampling is typically not performed on this stream and emission data collection methods will not be discussed in the remainder of this guide.

5.3.3 *Flash Tank Vent Gas*—Since the flash tank vent gas is often used as a fuel or stripping gas, sampling is typically not performed on this stream (2). Therefore, emission data collection methods will not be discussed in the remainder of this guide.

5.3.4 *Water and Hydrocarbon Condensate*—The water and hydrocarbon condensate collected from the reboiler still vent gas and condenser control technologies are typically routed to a three-phase separator (liquid hydrocarbon, water, and noncondensable gas). The noncondensable gas is recycled to the reboiler. Each liquid phase is pumped to a separate waste storage tank. Alternately, the combined liquid streams may be sent to a single storage tank. Problems associated with sampling these liquid streams include the following:

5.3.4.1 Collecting a representative sample of each liquid phase,

5.3.4.2 Accurately measuring the flow rates of the liquid

hydrocarbon and water streams since the separator discharge pumps may not run continuously. This is especially a problem when the liquids are not segregated in separate tanks.

5.3.5 *Waste Glycol/Reclaimer Waste*—Waste glycol is usually pumped to storage drums or tanks and then shipped off site for reclamation. The main problem associated with sampling this waste stream is sample homogeneity.

5.3.6 *Spent Filters*— Spent filters are typically stored in drums or dumpsters. The main problem associated with sampling this waste stream is obtaining a representative sample.

6. Approaches for Collecting Air Emission Data

6.1 *Introduction*— There are two often-used approaches for measuring the air emissions from the still vent stack: a rich/lean glycol mass balance (RL) and total capture stack condensation (TCC). Using the RL approach, emissions are calculated from the mass differences between the analytes in the rich and lean samples and the glycol flow rate. The glycol samples may be collected at atmospheric or pressurized operating conditions. Using the TCC approach, the total emissions to the atmosphere from the still vent are collected and separated into three phases (hydrocarbon liquid, water, and noncondensable gas) by chilling the still vent stream with an ice bath. Emission modeling programs such as GRI-GLYCalc³ can also be used to estimate emissions of BTEX and other VOC from the regenerator still vent gas. Some of the practical considerations recommended when using these sampling approaches are listed below as follows.

6.2 *Practical Considerations for RL Methods*—Glycol dehydration units have different types of hardware (for example, gas-driven or electric pumps, flash tanks, charcoal filters, heat exchangers) and variations in their glycol piping configurations that must be considered before sampling. Gas-driven pumps (for example, Kimray) inject gas into the rich glycol, that results in a larger noncondensable gas fraction in the rich glycol sample line. Some units are equipped with flash tanks, that will remove a portion of the noncondensable gas from the rich glycol line. Charcoal filters may be present and may absorb hydrocarbons from the glycol. Glycol dehydration units may have none, one, or a combination of several heat exchange systems found at different locations (for example, before or after flash tanks) on different units. (Several heat exchange systems found on glycol dehydration units include: concentric pipe rich/lean glycol; rich glycol passed through a coil in the surge tank; rich glycol preheated in the still; and concentric pipe lean glycol/outlet natural gas.) All of these factors play a role in the temperature, pressure, and the amount of gas/foam encountered during glycol sampling (3, 4).

6.2.1 The rich and lean glycol samples should be collected at locations where the glycol stream will be at the lowest possible temperature and pressure. A cooling coil should be used when collecting the rich glycol samples to minimize the loss of volatiles. Sampling points should not be at the top or bottom of filters or anywhere in the glycol stream where gas or liquid can accumulate.

6.2.2 The rich glycol should always be sampled at a point between the glycol pump and the reboiler. The sample point can be selected based on the flow chart in Fig. 2.

6.2.2.1 Sampling the rich glycol stream at units that have sampling points at high pressure (greater than 100 psig (689.5 kPa)), a high noncondensable gas flow rate (no flash tank), and a Kimray gas-driven pump results in a glycol sample that spews (especially in conjunction with the strokes of the Kimray pump) from the line as an aerosol.

6.2.2.2 Units that have rich glycol sample points at low pressure (less than 5 psig (34.5 kPa)), a low noncondensable gas flow rate (flash tank), an electric pump, and a cool glycol stream (glycol temperature less than 70°F (21.1°C)) can result in a viscous foamy glycol sample that flows very slowly through the cooling coil (a cooling coil is not necessary or practical in these situations).

6.2.3 If a charcoal filter is in line between the reboiler and the contactor, the lean glycol should be sampled at a point between the reboiler and charcoal filter. If a charcoal filter is not in line between the reboiler and the contactor, the lean glycol should be sampled at a point between the reboiler and the contactor. In both instances, the sample point should be selected on the low pressure side of the glycol pump. Also, sample points for the lean glycol may be very hot (>300°F (149°C)), especially if collected before any heat exchange device.

6.2.4 Kimray gas-driven pumps and electric pumps are used to determine the glycol flow rate. When Kimray glycol pumps are set up to run at or below their minimum recommended

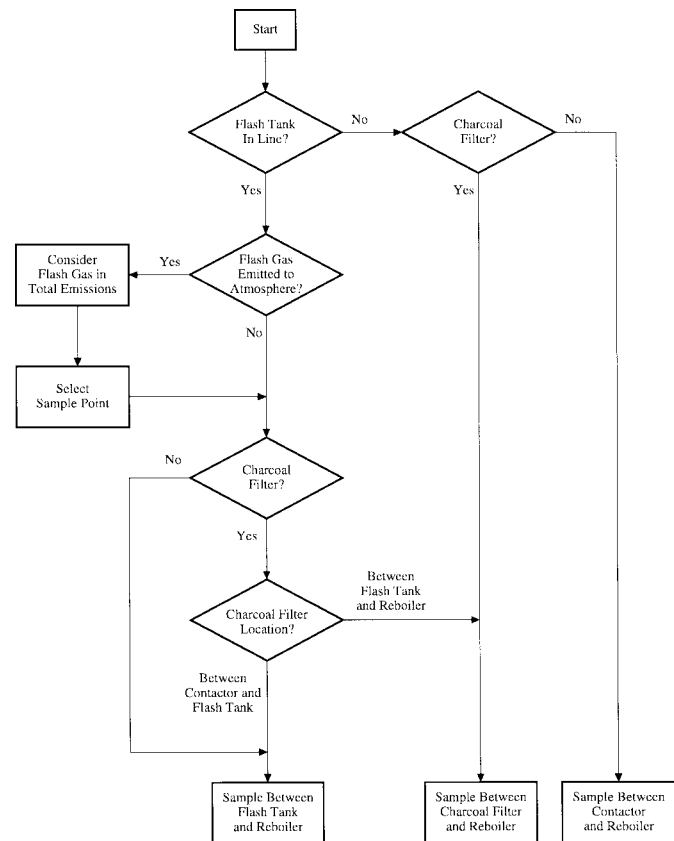


FIG. 2 Selection of the Rich Glycol Sample Port

³ GRI-GLY Calc is a registered trademark of Gas Research Institute, available from Radian International LLC, P. O. Box 201088, Austin, TX 78720-1088.

stroke rates, wide variations in glycol circulation rates may occur. Sampling and flow rate measurement should be conducted under conditions in which the glycol pumps are running within their recommended flow rate ranges.

6.2.5 Samples should be analyzed by GC/FID using EPA Methods 8020 and 8260⁴ or the direct injection approach outlined in Appendix X1 of this guide.

6.3 *Practical Considerations for TCC Methods*—There are many equipment variations to glycol dehydration units. The specific unit configuration and the process parameters must be considered before sampling to determine emissions from a specific unit. Units that do not have flash tanks or that have flash tanks maintained at low temperatures and high pressures may have condensable gas flow rates that could result in backpressure on the reboiler when the TCC apparatus is attached. When condensing the still vent stream on a glycol unit, one should make sure to minimize backpressure (preferably less than six inches of water column) on the reboiler. Depending on its size, the total capture device can normally only be used to condense the still vent stream on dehydration units drying less than 10 MMSCFD (3).

6.3.1 The TCC method should be carried out during both on and off reboiler firing cycles. Glycol reboiler firing cycles create positive and negative still vent flow. During reboiler firing, water and hydrocarbons are distilled from the glycol and their vapors create positive still vent flow. When the reboiler is off, the glycol begins to cool, and no more vapors are separated from the glycol. The existing vapors cool and their volume is reduced, which can result in reverse (negative) flow in the still vent line. Cyclic flow is common in glycol dehydration units and can be minimized or eliminated by maintaining a control of $\pm 2.5^{\circ}\text{F}$ (1.4°C) on the reboiler fire box. Due to the possibility of negative still vent flow, care must be taken when sampling the gas stream (noncondensable gas) to ensure that ambient air does not contaminate the sample.

6.3.2 When sampling with the TCC method, there are aqueous, liquid hydrocarbon, and gas phases that have to be sampled and measured. The total hydrocarbon emissions will be determined from the concentration of hydrocarbons in each phase coupled with the total volume of each phase collected during a given run time. If the ratio of water to condensed hydrocarbon is less than 16:1, then the contribution of the water phase to the total hydrocarbon emissions is probably negligible (less than 1 % of the emissions contained in the condensed hydrocarbon). The contribution of the noncondensable gas phase to total emissions is dependent on the noncondensable gas flow rate and composition; the noncondensable gas phase is often a significant portion of the total VOC emissions and may also contain significant amounts of BTEX on units without flash tanks.

6.3.3 Either a Tedlar bag or canister may be used in collecting the noncondensable gas sample. Tedlar bags are more widely used but are limited to short hold times due to the diffusion of the gases through the bag walls and the potential for light degradation. They are also difficult to ship because

they do not have fixed walls. Therefore, they are better suited for sites that are relatively close so that the Tedlar bags may be driven to the laboratory. By contrast, canisters are not used as widely and tend to be more expensive because of the cleaning procedures needed to reuse them. However, they are easily shipped and are well-suited for remote locations.

6.3.4 Liquid samples should be analyzed using EPA Methods 8020 and 8260⁴ or the analytical methods outlined in Ref (3). The gas samples should be analyzed using modified EPA compendium Method TO-14 or GPA Methods 2261 and 2286 as outlined in Ref (3).

6.4 The BTEX and other VOC emissions may be estimated using GRI-GLYCalc³ or other commercial software packages. The GRI-GLYCalc uses the inlet natural gas composition and process data, along with fundamental chemical engineering thermodynamics, to make the emissions estimates. (The natural gas may be collected and analyzed using the procedures outlined in GPA Methods 2166 and 2286 or modified EPA TO-14.) The GRI-GLYCalc³ tends to overpredict BTEX and VOC emissions, rather than underpredict, so emission estimates are conservatively high. Although this approach is less rigorous than the RL and TCC methods described above, it may be used as a rapid, inexpensive screening tool for determining which dehydration units are likely to be in compliance with applicable regulatory emissions levels.

7. Approaches for Collecting Liquid Waste Data

7.1 *Introduction*— The methods and practical considerations recommended when collecting samples from the liquid waste streams associated with glycol dehydrators are discussed as follows.

7.2 *Water and Hydrocarbon Condensate*—Direct pour/grab and scoop sampling techniques may be used to collect water and hydrocarbon condensate samples from waste storage tanks (9).

7.2.1 Direct pour sampling involves the transfer of a waste sample from the source directly into the sample container. This collection method should be used when a discharge port is available on the tank, and when there is no means of compositing the waste stream. Prior to collecting the sample, the port and related piping should be purged to ensure that the sample is representative of the material in the vessel. Small containers may be sampled by directly pouring from the container into the sample bottles. Sample homogeneity is a potential concern.

7.2.2 Direct grab sampling consists of dipping a borosilicate beaker or weighted sample bottle into a process or storage vessel. The weighted sample bottle typically consists of a glass or plastic bottle with a sinker and stopper, in addition to a line that is used to lower, raise, and open the bottle. The weighted bottle should be lowered into a tank to the desired level or layer and then opened and filled. Multiple random samples should be composited into a 5-gal (18.9 L) carboy and distributed to the appropriate sampling containers.

7.2.3 Disposable scoops should be used to collect samples of high-viscosity liquid wastes. These samples should be composited directly into wide-mouth bottles by collecting several scoops of material.

7.2.4 Field blank samples should be collected on site when possible.

⁴ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20036.

7.2.5 Water and hydrocarbon condensate samples should be analyzed using EPA Methods 8020 and 8260 or the analytical methods outlined in Ref (3). Toxicity Characteristic Leaching Procedure (TCLP) testing, as described in 40 CFR Part 261 Appendix II, should be conducted if RCRA toxicity data are needed.

7.3 *Waste Glycol/Reclaimer Waste*—Direct pour/grab and composite liquid sampling techniques (COLIWASA) may be used to collect the waste glycol/reclaimer waste samples from waste storage tanks or drums (9).

7.3.1 Waste glycol stored in tanks should be sampled using the direct pour/grab techniques discussed in 8.2.1 and 8.2.2.

7.3.2 Waste glycol stored in drums should be sampled using a composite liquid sampler (COLIWASA). This device typically consists of a 4-ft (1.22-m)-long glass or PVC tube having an inside diameter of approximately 1.25 in. (31.75 mm), with a 0.25-in. (6.35 mm) diameter stainless steel (or TFE-fluorocarbon) rod with attached stoppers passing down the center through the length of the tube. The COLIWASA should be used by opening the stoppered lower end and slowly lowering the tube into the liquid. As the tube passes through the drum, a composite sample is collected over the length of the drum. When the bottom of the drum is reached, the stopper should be pressed back into the tube openings, thereby trapping the sample within the tube. At this point, the COLIWASA

contains a composite sample of the drum. When the COLIWASA is withdrawn, it may be emptied into the sample container. When compositing from multiple drums, each sample container should be proportionately filled from each drum.

7.3.3 Field blank samples should be collected on site when possible.

7.3.4 These waste samples should be analyzed using the TCLP procedures described in 40 CFR, Part 261, Appendix II.⁴

8. Approach for Collecting Solid Waste Data

8.1 *Introduction*— The methods and practical considerations recommended when collecting samples from the solid waste stream associated with glycol dehydrators are discussed as follows.

8.2 Filters should not be removed from a unit until differential pressure indicates that the filter should be removed. Care should be used when removing a filter from a high-pressure application.

8.3 The spent filters should be cut into pieces using a hack saw and scissors and composited. If possible, the composite should be made from three different sample filters (9).

8.4 These samples should be analyzed using the TCLP procedures described in 40 CFR, Part 261, Appendix II.⁴

APPENDIX

(Nonmandatory Information)

X1. ATMOSPHERIC RICH/LEAN GLYCOL METHOD STANDARD PROCEDURE

X1.1 Purpose

X1.1.1 The purpose is to determine still vent emissions from triethylene glycol (TEG) dehydration units. Still vent emissions are calculated from the mass differences between the analytes in the atmospheric rich and lean glycol samples and the glycol flow rate.

X1.2 Scope and Applicability

X1.2.1 *Scope*—A procedure for collecting and analyzing samples taken from natural gas dehydration units that use TEG as the desiccant. Determining the glycol flow rate, calculating still vent emissions from a dehydration unit, and using VOC emission correction factors for units with high gaseous non-condensable still vent flow rates are also covered.

X1.2.2 *Applicability*— Still vent emissions may be estimated for benzene, toluene, ethylbenzene, and the xylenes (BTEX), as well as *n*-hexane, 2,2,4-trimethylpentane, C₅ to C₁₀ normal alkanes, cyclohexane, and total hydrocarbons.

X1.3 Safety

X1.3.1 Glycol samples may be under high pressure (potentially greater than 1000 psig (6895 KPa)) and may be hot (380°F (193°C)). Samples may have high levels of benzene and other aromatic and aliphatic hydrocarbons that pose exposure hazards. Natural gas present in the glycol sample

lines is a potential fire or explosion hazard.

X1.4 Glycol Sampling Procedure

X1.4.1 Obtain atmospheric rich and lean glycol samples from natural gas glycol dehydration units. Collect these samples in 40-mL VOA vials at identified points on a glycol dehydration unit. The results of the rich and lean sample analysis, along with the glycol circulation rate, are used to perform a mass balance of air toxic emissions (*n*-hexane, benzene, toluene, ethylbenzene, xylenes, and other volatile organic compounds VOCs) from the glycol dehydrator still vent.

X1.4.2 *Identification of a Glycol Sampling Location*— Collect both rich and lean glycol samples at locations where the glycol stream will be at the lowest possible temperature and pressure. Sampling points should not be at the top or bottom of filters or anywhere in the glycol stream where gas or liquid can accumulate.

X1.4.3 *Rich Glycol:*

X1.4.3.1 *Step 1*—Always select a sample point between the glycol pump and the reboiler.

X1.4.3.2 *Step 2*—Select a sample point based on the flow chart in Fig. X1.1.

X1.4.4 *Lean Glycol:*

X1.4.4.1 *Step 1*—Determine if a charcoal filter is in line

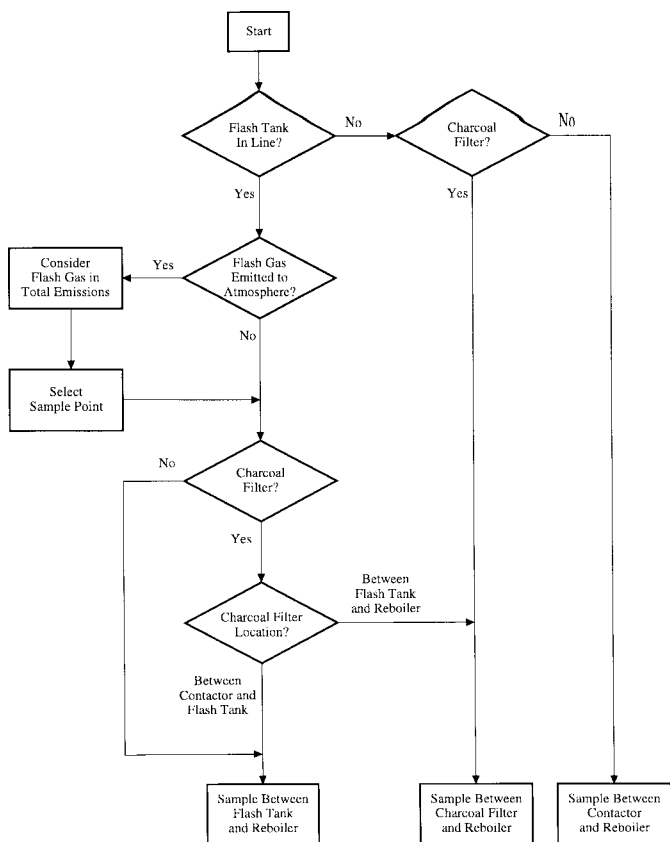


FIG. X1.1 Selection of the Rich Glycol Sample Port

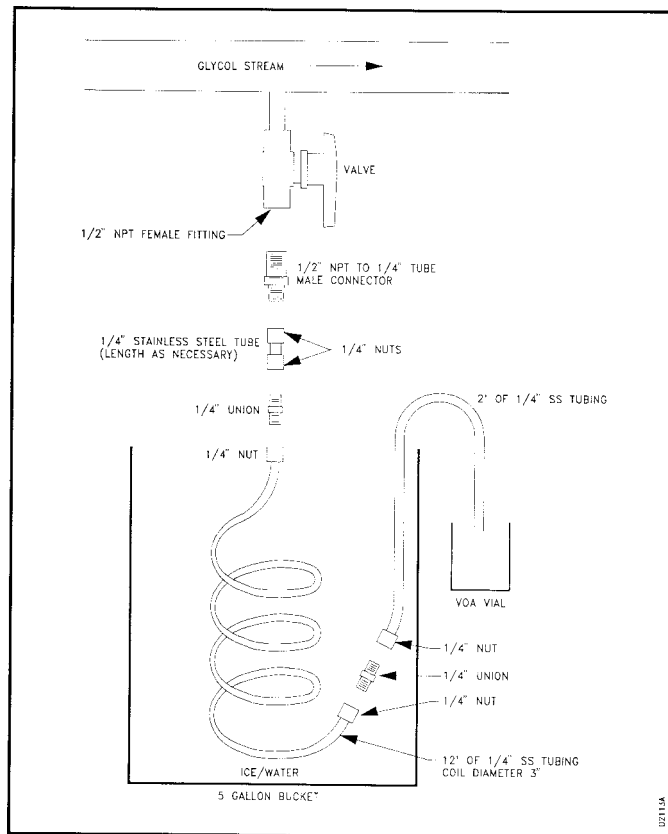


FIG. X1.2 ARL Sampling System

between the reboiler and the contactor. Proceed to Step 2 (X1.4.4.2) if a charcoal filter is in line between the reboiler and the contactor. Proceed to Step 3 (X1.4.4.3) if a charcoal filter is not in line between the reboiler and the contactor.

X1.4.4.2 *Step 2*—Select a lean glycol sample point between the reboiler and the charcoal filter. Preferably select a sample point on the low-pressure side of the glycol pump.

X1.4.4.3 *Step 3*—Select a lean glycol sample point between the reboiler and the contactor. Preferably select a sample point on the low-pressure side of the glycol pump.

X1.4.5 *Sampling Valves, Lines, and Connections*—After identifying the appropriate sample points, modify them so that the glycol stream may be cooled and sampled at atmospheric pressure. Cooling the glycol sample is not necessary if the temperature of the glycol is less than 70°F (21.1°C).

X1.4.5.1 *Step 1*—The glycol stream lines on most glycol dehydration units are generally 1-in. (25.4-mm) pipe and have National Pipe Thread (NPT) fittings. Adapt the identified sample port from the NPT fitting to a 1/4-in. (6.35-mm)-Swagelok male fitting.

X1.4.5.2 *Step 2*—Connect a sampling coil made from approximately 12 ft (3.66 m) of 1/4-in. (6.35-mm)-copper or stainless steel tubing to the 1/4-in. (6.35-mm)-Swagelok sample valve. See Fig. X1.2.

X1.4.6 *Label the VOA Vials For Glycol Sample Collection*—Before collecting the samples, affix a label to the VOA vial that states the date, sample point, sample type (rich or lean glycol sample), and a unique identification number. Once the label is attached to the VOA vial, cover it with a clear

tape. Select the writing utensil carefully, since glycol dissolves ink and felt markings. Pencil, or preferably a tested permanent marker (one that does not leave a glycol soluble mark), works best. The label should be completely filled out, affixed to the vial, and covered with clear tape before sampling begins.

X1.4.7 *Collection of Glycol Samples:*

X1.4.7.1 *Step 1*—Immerse the 1/4-in. (6.35-mm)-sampling coil in an ice/water bath contained in a 5-gal (18.9-L) bucket.

X1.4.7.2 *Step 2*—Open the glycol sampling port and purge a stream of glycol through the sampling coil for two minutes. Rich glycol sample generally sprays from the sample line as a foamy aerosol.

X1.4.7.3 *Step 3*—Place a 40-mL glass VOA vial under the flow of glycol and fill the vial to overflowing.

X1.4.7.4 *Step 4*—Place the cap, with the septum TFE-fluorocarbon side down, on the VOA vial immediately after the glycol begins to overflow the vial. Do not overtighten the cap. Trapped gases (headspace) can generally be observed in the vials. Do not try to eliminate the trapped gases in the vials because this will result in loss of additional target analytes from the glycol.

X1.4.8 *Shipment of VOA Vials Containing Glycol Samples*—Place the glycol samples in a cooler on ice and keep them at about 39°F (4°C). Complete a chain of custody form and ship the samples under a chain of custody to a laboratory for analysis.

X1.4.9 *Glycol Circulation Rate:*

X1.4.9.1 *Kimray Gas-Driven Pumps*—Determine the glycol circulation rate by counting pump strokes for a set period of

time and converting the stroke rate to a flow rate using Table X1.1. The time required for 25 strokes (strokes should be counted for at least 2 min) should be recorded and then the counted number of strokes per minute converted to a glycol circulation rate. Use this flow rate in all calculations requiring the glycol circulation rate.

X1.4.9.2 Example—Calculate the glycol flow rate in gallons (litres) per hour for a Kimray Model 20015SC pump in which 22 strokes were counted in 2 min 15 s as follows:

2 min 15 s	= 2.25 min
22 strokes/2.25 min	= 9.8 strokes/min
(9.8 strokes/min) × (60 min/h)	= 588 strokes/h
(588 strokes/h) × (0.114 gal/stroke (L/stroke))	= 67 gal/h (253.6 L/h)

X1.4.10 Electric Pumps—Obtain the glycol circulation rate from the manufacturer's data or calculate it as follows.

X1.4.10.1 Step 1—Determine the number of displacement pistons (*ndp*).

X1.4.10.2 Step 2—Determine the radius (*r*) of the pistons in inches.

X1.4.10.3 Step 3—Determine the stroke length (*h*) of the pistons in inches.

X1.4.10.4 Step 4—Determine the revolutions per minute (*rpm*) of the pump drive wheel.

X1.4.10.5 Step 5—Calculate the pumps glycol displacement in gallons (litres) per revolution (*gpr*):

$$(gpr) = (ndp)(\pi r^2 h)(4.329 \times 10^{-3} \text{ gal/in.}^3 (10^{-6} \text{ L/mm}^3)) \quad (\text{X1.1})$$

X1.4.10.6 Step 6—Calculate the glycol flow rate in gallons (litres) per hour (*gph*):

$$(gph) = (rpm)(gpr)(60 \text{ min/h})(\text{pump efficiency}) \quad (\text{X1.2})$$

If the pump efficiency is not known use 95 %.

X1.4.10.7 Example—Calculate the glycol flow rate in gallons per hour for an electric pump with two pistons. Each piston has a radius of 0.5 in. and a stroke length of 2.25 in. (57.15 mm). The pump speed is 160 rpm's:

$$2 \times (\pi \times (0.5 \text{ in.})^2 \times 2.25 \text{ in. (57.15 mm)}) \times 4.329 \times 10^3 \text{ gal/in.}^3 \quad (\text{X1.3})$$

$$(10^{-6} \text{ L/mm}^3) = 0.015 \text{ gpr}$$

$$160 \text{ rpm} \times 0.015 \text{ gpr} \times 60 \text{ min/h} \times 0.95 \text{ efficiency} = 137 \text{ gph}$$

X1.5 Analytical Conditions and Glycol Analysis

X1.5.1 Use gas chromatographic systems with flame ionization detectors to quantitate the BTEX target analytes, as well as cyclohexane, 2,2,4-trimethylpentane (*isooctane*), C₅ to C₁₀

normal alkanes, and total hydrocarbons (see Table X1.2). Use a gas chromatograph equipped with a split/splitless injector and a capillary column to analyze the liquid samples. Quantitation of the target and nontarget analytes is based on individual response factors. Calibration procedures at the end of this section. Use a response factor for *n*-hexane to quantify the unidentified hydrocarbons. Method interferences are discussed in X1.6.

X1.5.2 Preparation of Stock Solution:

X1.5.2.1 Step 1—Add approximately 10 mL of dichloromethane to a 25-mL volumetric flask.

X1.5.2.2 Step 2—Add 500 µL of each target analyte (analytes need to be at room temperature), in order of descending boiling point, to the 25-mL volumetric flask with a 1-mL gas-tight syringe keeping the tip of the syringe needle below the surface of the diluent.

X1.5.2.3 Step 3—Dilute the solution in the 25-mL volumetric flask to volume with dichloromethane, and cap and shake the flask.

X1.5.2.4 Step 4—Verify the quality of the stock solution by comparison of the standards made from the stock solution with a second reference standard (see X1.5.4.4).

X1.5.3 Preparation of Primary Standards:

X1.5.3.1 Step 1—Prepare five standards, each at a different concentration, by removing (with a gas-tight syringe) an aliquot from the stock solution and injecting the aliquot below the surface of the dichloromethane in 10-mL volumetric flasks:

- Use 1000 µL of stock solution in Flask 1;
- Use 400 µL of stock solution in Flask 2;
- Use 100 µL of stock solution in Flask 3;
- Use 50 µL of stock solution in Flask 4; and
- Use 10 µL of stock solution in Flask 5.

X1.5.3.2 Step 2—Dilute the contents in each flask to volume; cap them; shake them to ensure mixing.

X1.5.3.3 Step 3—Remove approximately 1-mL aliquots from the flasks and place each in labeled GC crimp-top vials. Cap the crimp-top vials, and use them in X1.5.4 and X1.5.5.

X1.5.4 Calibration Procedures—Use the primary standards prepared in X1.5.3 to obtain a calibration factor for each target analyte. The concentrations of the primary standards should bracket the range of concentrations found in glycol samples.

X1.5.4.1 Step 1—Inject 1 µL of each primary standard into a GC/FID system.

X1.5.4.2 Step 2—Calculate a calibration factor (*CF*) for each analyte at each standard concentration:

$$(CF) = (\text{amount injected in mg/L})/(\text{total area of peak}) \quad (\text{X1.4})$$

TABLE X1.1 Glycol Flow Rates

Pump	Strokes/Minute	Glycol Output Strokes/Gallon (Litres)	Glycol Output Gallons (Litres)/Stroke
315PV	20 to 100	435 (114.9)	0.0023 (0.0087)
1715PV	8 to 40	59 (15.59)	0.017 (0.0642)
4015PV	12 to 40	59 (15.59)	0.017 (0.642)
9015PV	12 to 40	26.3 (6.948)	0.038 (0.144)
21015PV	10 to 32	9 (2.378)	0.111 (0.421)
45015PV	10 to 28	3.5 (0.925)	0.283 (1.082)
2015SC	5 to 55	147 (38.83)	0.0068 (0.0258)
5015SC	10 to 50	52 (13.74)	0.0193 (0.0728)
10015SC	10 to 48	25 (6.604)	0.040 (0.151)
20015SC	10 to 40	8.8 (2.325)	0.114 (0.430)

TABLE X1.2 Analytical Conditions for the Analysis of Liquid Samples

Instrument	Hewlett-Packard 5880
Detector	FID
Injection system	capillary; split 50 to 1
Column	60-m × 0.32-mm inside diameter 3.0-µ film Restek RTX ₁
Carrier gas	helium at 20 psig
Carrier gas flow rate	~3 mL/min
Make-up gas	helium at 30 mL/min
Temperature program	40°C for 2 min; programmed at 8°C/min to 225°C, final hold 10 min
Injector temperature	275°C
Detector temperature	300°C
Injection volume	1 µL

X1.5.4.3 *Step 3*—Calculate average calibration factor (\overline{CF}) for each analyte. If the percent relative standard deviation (% RSD) of the \overline{CF} s is less than 20 % over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve:

$$(\% \text{ RSD}) = [(standard\ deviation)/(\overline{CF})] \times 100 \quad (X1.5)$$

X1.5.4.4 *Step 4*—Verify the validity of the calibration standards by injecting an independent mid-level standard (purchased from a second-source) once following each multi-point calibration using a subset of the target analytes. If the response for the independent calibration standard varies more than $\pm 10\%$ of the expected value, take corrective action to verify the accuracy of the source materials.

X1.5.5 Calibration Control Checks:

X1.5.5.1 Verify the working calibration factor by injecting a mid-level calibration standard at the beginning and end of each working day or analysis sequence. If the response for any target analyte varies from the predicted response by more than $\pm 15\%$ (relative percent difference (RPD)), conduct a second analysis of the calibration standard. If two calibration checks in a row vary from the predicted response by more than $\pm 15\%$, conduct a system check.

X1.5.5.2 Make sure gas flows have not changed, and if they have, reset to initial conditions. Place a new septum in the injector port. Cleaning the injector and detector may also be necessary. After performing the system check, rerun the calibration check, and if the response still varies by more than 15 %, prepare a new calibration factor (or curve).

$$RPD = [(\overline{CF} - CF \text{ for calibration check})/(\overline{CF})] \times 100 \quad (X1.6)$$

X1.5.6 *Preparing, Analyzing, and Screening Glycol Samples*—Dilute glycol samples with dichloromethane before analyzing them by direct injection into a GC/FID system. Do a preliminary analysis on one rich and one lean glycol sample to make sure that the concentrations of the target analytes in the glycol sample are bracketed by the range of standard concentrations used to generate the standard curve. If the concentrations of the target analytes fall outside of the concentrations used to generate the standard curve, either use a different dilution ratio for the sample or add another point to the standard curve. Spike at least 10 % of the glycol samples analyzed with a subset of the target analytes, such as *n*-hexane, benzene, toluene, and *n*-octane. The concentrations of the analytes determined by the preliminary analysis can be used to calculate the spike solution (see X1.5.8). The concentrations of the analytes determined by the preliminary analysis can be used to calculate the spike solution.

X1.5.7 Dilute and Analyze the Glycol Samples:

X1.5.7.1 *Step 1*—Allow the glycol sample to warm to room temperature before dilution.

X1.5.7.2 *Step 2*—Rinse a 1-mL volumetric flask five times with 1-mL aliquots of dichloromethane. Add approximately 250 μL of dichloromethane to a 1-mL volumetric flask.

X1.5.7.3 *Step 3*—Rinse a 1-mL gas-tight syringe with 3 aliquots of the sample by inserting the needle of the syringe through the septum on a VOA vial containing the glycol sample. Withdraw about 600 μL of sample into the syringe and remove the syringe from the VOA vial. Discharge the sample

from the syringe into a waste container.

X1.5.7.4 *Step 4*—Insert the needle of the 1-mL gas-tight syringe through the septum on a VOA vial containing the glycol sample. Withdraw about 600 μL of sample into the syringe and remove the syringe from the VOA vial. Hold the syringe upright at eye level and adjust the plunger so that 500 μL of glycol sample remains in the syringe.

X1.5.7.5 *Step 5*—Place the needle of the syringe that contains the glycol sample under the surface of the 250 μL of dichloromethane in the 1-mL volumetric flask. Slowly introduce the sample into the solvent.

X1.5.7.6 *Step 6*—Repeat X1.5.7.3 and X1.5.7.4 on either 10 % of the samples or at least on one sample per set of analysis. Also repeat X1.5.7.3 and X1.5.7.4 on either 10 % of the samples or at least on one sample per set of analysis for use in the spike dilution process (see X1.5.8).

X1.5.7.7 *Step 7*—After introduction of the sample into the volumetric flask, add dichloromethane to fill the volumetric flask to volume.

X1.5.7.8 *Step 8*—Cap the volumetric flask and shake it briefly.

X1.5.7.9 *Step 9*—Remove the diluted sample from the volumetric flask with a disposable pipet and place it in a labeled crimp top vial. Cap the crimp top vial.

X1.5.7.10 *Step 10*—Analyze 1 μL of the diluted sample by GC/FID. See X1.7 for interferences.

X1.5.7.11 *Step 11*—Rinse the syringe and volumetric flask five times with 1 mL of dichloromethane after each use. After every ten samples, analyze (by GC/FID) the last dichloromethane rinse from washing the volumetric flask and syringe to see if cross contamination is occurring.

X1.5.7.12 *Step 12*—Calculate the concentration of the analytes in the diluted glycol sample. Multiply the average calibration factor for each analyte by the peak area for that analyte.

X1.5.7.13 *Step 13*—Calculate the concentration of the analytes in the original glycol sample. Multiply the concentration of each analyte in the diluted glycol sample by the dilution factor (for example, two if a 1:1 dilution was used).

X1.5.7.14 *Step 14*—Calculate the relative percent difference (RPD) for the analytical duplicates. The RPD for the analytical duplicates should be $\pm 10\%$.

$$RPD = \frac{|(C1 - C2)|}{(C1 + C2)/2} \times 100 \quad (X1.7)$$

where:

C 1 = concentration of the first sample, and

C 2 = concentration of the duplicate sample.

X1.5.8 *Glycol Spike Dilution Process*—Spike the samples during the dilution process so that the concentration of the target analytes is approximately twice that of the original sample.

X1.5.9 Preparing Spike Solution:

X1.5.9.1 *Step 1*—Prepare the spike solution based on adding 100 μL of a spike solution into the 1-mL volumetric flask used during glycol sample dilution.

X1.5.9.2 *Step 2*—Use *n*-hexane, benzene, toluene, and *n*-octane as the target analytes to prepare the spike solution.

X1.5.9.3 *Step 3*—Calculate the concentration of the spike solution based on the concentrations of target analytes in the diluted glycol sample (see X1.5.7.12).

$$C_s = \frac{(Cd \times Vd)}{V_s} \quad (X1.8)$$

where:

C_s = concentration of the spike solution, mg/L;
 Cd = concentration of the analytes in the diluted sample,
 Vd = total volume of the diluted sample, mL, and
 V_s = volume of the spike solution to be added during the dilution process, mL.

X1.5.9.4 *Step 4*—For example: A diluted glycol sample (see X1.5.7.12) that contained the following four analytes, *n*-hexane at 48 ppm, benzene at 1854 ppm, toluene at 1462 ppm, and *n*-octane at 36 ppm, prepare the following spike solution. In the following order, add 3 μ L of *n*-octane, 90 μ L of toluene, 110 μ L of benzene, and 4 μ L of *n*-hexane to approximately 5 mL of dichloromethane in a 10-mL volumetric flask. Dilute the resulting solution to a total volume of 10 mL with dichloromethane.

X1.5.10 *Spike Dilution Process:*

X1.5.10.1 *Step 1*—Add approximately 250 μ L of dichloromethane to a 1-mL volumetric flask.

X1.5.10.2 *Step 2*—Rinse a 1-mL gas-tight syringe with three aliquots of the sample by inserting the needle of the syringe through the septum on a VOA vial containing the glycol sample. Withdraw about 600 μ L of sample into the syringe and remove the syringe from the VOA vial. Discharge the sample from the syringe into a waste container.

X1.5.10.3 *Step 3*—Remove a 500- μ L aliquot of the glycol sample from the VOA vial by taking the aliquot through the septum with the 1-mL gas-tight syringe.

X1.5.10.4 *Step 4*—Place the tip of the syringe needle under the surface of the 250 μ L of dichloromethane in the 1-mL volumetric flask. Slowly introduce the sample into the solvent.

X1.5.10.5 *Step 5*—Remove a 100- μ L aliquot of the spike solution from the 10-mL volumetric flask prepared above.

X1.5.10.6 *Step 6*—Place the needle from the syringe that contains the spike solution under the surface of the dichloromethane in the 1-mL volumetric flask from X1.5.10.3. Slowly introduce the sample into the solvent.

X1.5.10.7 *Step 7*—Dilute the resulting solution in the 1-mL volumetric flask to volume. Place it in a crimp top vial, and cap the vial.

X1.5.10.8 *Step 8*—Analyze 1 μ L of the spiked sample by GC/FID. See X1.6 for interferences.

X1.5.10.9 *Step 9*—Calculate the concentration of the spiked analytes in the diluted spiked sample. Multiply the average calibration factor for each analyte by the peak area for that analyte.

X1.5.10.10 *Step 10*—Calculate the percent spike recovery.

$$\% \text{ rec} = \frac{(S_s - S_d)}{S_f} \times 100 \quad (X1.9)$$

where:

$\% \text{ rec}$ = percent recovery;
 S_s = diluted spiked sample result, mg/L,
 S_d = diluted glycol sample result, mg/L, and

S_f = amount of spike added, mg/L.

X1.5.11 *Spike Solution Analytical Checks*—Perform analytical checks by using the spike solution prepared above.

X1.5.11.1 *Step 1*—Add approximately 500 μ L of dichloromethane to a 1-mL volumetric flask.

X1.5.11.2 *Step 2*—Add 100 μ L of the spike solution to the volumetric flask with the syringe needle tip under the surface of the solvent.

X1.5.11.3 *Step 3*—Dilute the resulting solution to volume with dichloromethane.

X1.5.11.4 *Step 4*—Analyze 1 μ L of the solution by GC/FID.

X1.5.11.5 *Step 5*—Calculate the concentration of the analytes in the diluted spike solution. Multiply the average calibration factor for each analyte by the peak area for that analyte.

X1.5.11.6 *Step 6*—Calculate the concentration of the analytes in the spike solution. Multiply the concentration of each analyte in the diluted sample by the dilution factor (ten if a 1:10 dilution was used).

X1.5.11.7 *Step 7*—Calculate the relative percent difference (RPD) for the spike solution checks:

$$RPD = \frac{|(C_s - C_t)|}{(C_s + C_t)/2} \times 100 \quad (X1.10)$$

where:

C_s = concentration of spike solution, mg/L, and
 C_t = theoretical concentration of the spike solution, mg/L.

X1.6 Interferences

X1.6.1 *Autosamplers*—Set autosamplers used for glycol injections into the GC to account for the viscosity of the glycol. When autosamplers are set improperly, two problems are encountered: boiling point discrimination when low boiling diluents are used, and incomplete filling of the syringe when samples are withdrawn from the vial. Both of these problems can be detected by spiking a glycol sample with hexane and benzene at levels that will approximately double their concentrations, followed by analyzing the spiked sample.

X1.6.2 *Ethylene and Diethylene Glycol*—Triethylene glycol (TEG) samples from some glycol units contain diethylene glycol or ethylene glycol, or both, that can be at a high enough concentration to interfere with the quantitation of analytes of interest under certain GC conditions (interferences caused by coelution with analytes of interest). Note that ethylene glycol by itself is not soluble in dichloromethane, that is the diluent used for TEG analysis.

X1.7 Still Vent Emission Calculations

X1.7.1 *Still Vent Emissions Based on Rich/Lean Glycol Samples*—Calculate still vent emissions in tons per year (tpy) from glycol dehydration units by using both field and analytical data.

X1.7.1.1 *Step 1*—Get the average glycol flow rate in gallons (litres) per hour (gph).

X1.7.1.2 *Step 2*—Get the analyte concentrations in the rich and lean glycol samples in milligrams/Litre.

X1.7.1.3 *Step 3*—Average the results from the duplicate

analyses to determine a single value for the sample concentrations. Average the duplicate sample results to report a single value for each run.

X1.7.1.4 Step 4—Determine compound emissions directly from the concentrations in rich and lean glycol samples and the glycol flow rate:

$$\begin{aligned} \text{compound emissions, tpy} = & \quad (X1.11) \\ & (\text{analyte concentration in rich glycol, mg/L} - \\ & \text{analyte concentration in lean glycol, mg/L}) \times \\ & (\text{average glycol flow, gph}) \times \left(\frac{3.7856 \text{ L}}{1 \text{ gal}} \right) \times \left(\frac{1 \text{ lb}}{453.600 \text{ mg}} \right) \times \\ & \left(\frac{1 \text{ ton}}{2000 \text{ lb}} \right) \times \left(\frac{8760 \text{ h}}{1 \text{ year}} \right) \end{aligned}$$

X1.7.2 VOC Still Vent Emissions Correction Factors—Calculate the VOC still vent emissions for glycol dehydration units that utilize stripping gas or that do not have flash tanks.

X1.7.2.1 Step 1—Determine the stripping gas (SG) losses in:

$$SG, \text{ tpy} = (0.0001156) \times (\text{flow, SCF/h}) \sum C_i MW_i \quad (X1.12)$$

where:

flow = stripping gas flow, SCF/h,

C_i = inlet natural gas concentration of Compound i , mole percent; and

MW_i = molecular weight of the compound.

X1.7.2.2 Step 2—Determine the flashing (F) and pump (P) gas losses in tpy :

$$FP, \text{ tpy} = GCirc \sum C_i CF_i \quad (X1.13)$$

where:

$GCirc$ = glycol circulation rate in gal (L)/hour,

C_i = inlet natural gas concentration of Compound i , mole percent, and

CF_i = correction factor for Compound i taken from Tables X1.3-X1.10. Use Table X1.3 for electric glycol pumps and Tables X1.7-X1.10 for Kimray glycol pumps.

X1.7.2.3 Step 3—Calculate still vent VOC emissions in tpy:

$$VOC, \text{ tpy} = ARL, \text{ tpy} + SG, \text{ tpy} + FP, \text{ tpy} \quad (X1.14)$$

X1.8 Materials and Apparatus

X1.8.1 Sampling Glycol Streams:

X1.8.1.1 Various Swagelok Fittings— $\frac{1}{4}$ -in. (6.35 mm)-unions, $\frac{1}{4}$ -in. (6.35 mm)-front and back ferrules, $\frac{1}{4}$ -in. (6.35 mm)-union elbows, $\frac{1}{4}$ -in. (6.35 mm)-nuts, $\frac{1}{4}$ -in. (6.35 mm)-port connectors, $\frac{1}{2}$ -in. (12.7 mm) and $\frac{3}{8}$ -in. (9.525 mm)-reducing port connectors to $\frac{1}{4}$ in. (6.35 mm), $\frac{1}{4}$ -in. (6.35 mm)-tube Cajon fractional tube adaptor to male NPT ($\frac{3}{8}$ in. (9.525 mm), $\frac{1}{2}$ in. (12.7 mm), $\frac{3}{4}$ in. (19.05 mm), $\frac{5}{8}$ in. (15.875 mm),

X1.8.1.2 Twenty-five feet (3.66 m) of $\frac{1}{4}$ -in. (6.35 mm)-stainless steel tubing,

X1.8.1.3 Ten-feet (3.05 m) coil of $\frac{1}{4}$ -in. (6.35 mm)-stainless steel tubing (easily prepared by coiling a 12-ft (3.66 m) piece of $\frac{1}{4}$ -in. (6.35 mm)-tubing around a 3-in. (76.2 mm)-piece of pipe),

X1.8.1.4 VOA vials, 40 mL,

X1.8.1.5 Five-gallon (18.9 L) bucket for immersing cooling coil,

X1.8.1.6 Sample labels,

X1.8.1.7 Clear tape,

X1.8.1.8 Gallon-size plastic storage bags,

X1.8.1.9 Hard-shell coolers,

X1.8.1.10 Pens and markers, and

X1.8.1.11 Chain of custodies/paperwork for samples.

X1.8.2 Sample Preparation:

X1.8.2.1 Gas-Tight Syringes—1 mL, 500, 250, 100, and 10 μ L.

X1.8.2.2 Volumetric Flask—50, 25, 10, and 1 mL.

X1.8.2.3 Solvents—Dichloromethane.

X1.8.2.4 Standards—99 + % pure n -pentane, n -hexane, n -heptane, cyclohexane, $isooctane$, n -octane, n -nonane, n -decane, benzene, toluene, ethylbenzene, m -xylene, p -xylene, 98 % + pure o -xylene.

TABLE X1.3 Pentane (C3) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0073	0.0095	0.0112	0.0142	0.0151	0.0164	0.0163	0.0166	0.0161
50 (10.0)	0.0065	0.0086	0.0101	0.0130	0.0138	0.0151	0.0152	0.0156	0.0153
60 (15.6)	0.0058	0.0078	0.0092	0.0119	0.0127	0.0140	0.0143	0.0147	0.0146
70 (21.1)	0.0053	0.0070	0.0084	0.0109	0.0118	0.0131	0.0134	0.0139	0.0139
80 (26.7)	0.0048	0.0065	0.0078	0.0101	0.0109	0.0122	0.0126	0.0132	0.0133
90 (32.2)	0.0044	0.0060	0.0072	0.0094	0.0102	0.0114	0.0119	0.0125	0.0127
100 (37.8)	0.0041	0.0055	0.0066	0.0088	0.0096	0.0108	0.0113	0.0119	0.0121
110 (43.3)	0.0038	0.0051	0.0062	0.0082	0.0090	0.0102	0.0107	0.0113	0.0116
120 (48.9)	0.0035	0.0048	0.0058	0.0077	0.0085	0.0096	0.0102	0.0108	0.0111
130 (54.4)	0.0033	0.0045	0.0055	0.0072	0.0080	0.0092	0.0097	0.0104	0.0107
140 (60.0)	0.0031	0.0042	0.0052	0.0069	0.0076	0.0088	0.0093	0.0100	0.0103

^A Correction = (mole % C3 in gas) \times (glycol circulation, gph) \times CF.

^B If propane mole % is not known, use 4.2 %.

TABLE X1.4 Pentane (C4) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0119	0.0152	0.0172	0.0220	0.0224	0.0239	0.0228	0.0226	0.0211
50 (10.0)	0.0105	0.0135	0.0154	0.0198	0.0204	0.0220	0.0213	0.0213	0.0202
60 (15.6)	0.0093	0.0120	0.0139	0.0180	0.0187	0.0204	0.0201	0.0202	0.0193
70 (21.1)	0.0083	0.0109	0.0126	0.0165	0.0172	0.0189	0.0189	0.0193	0.0184
80 (26.7)	0.0075	0.0098	0.0115	0.0151	0.0160	0.0177	0.0177	0.0183	0.0178
90 (32.2)	0.0068	0.0090	0.0106	0.0140	0.0148	0.0165	0.0167	0.0173	0.0171
100 (37.8)	0.0062	0.0083	0.0097	0.0130	0.0138	0.0155	0.0158	0.0165	0.0164
110 (43.3)	0.0057	0.0076	0.0091	0.0121	0.0130	0.0146	0.0150	0.0158	0.0157
120 (48.9)	0.0053	0.0070	0.0084	0.0113	0.0122	0.0139	0.0143	0.0151	0.0151
130 (54.4)	0.0049	0.0066	0.0079	0.0107	0.0115	0.0132	0.0205	0.0145	0.0146
140 (60.0)	0.0046	0.0062	0.0074	0.0101	0.0110	0.0125	0.0130	0.0139	0.0141

^A Correction = (mole % C4 in gas) × (glycol circulation, gph) × CF .

^B If butanes mole % is not known, use 2.1 %.

TABLE X1.5 Pentane (C5) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0337	0.0411	0.0449	0.0666	0.0652	0.0756	0.0697	0.0713	0.0644
50 (10.0)	0.0280	0.0346	0.0379	0.0571	0.0566	0.0665	0.0618	0.0650	0.0592
60 (15.6)	0.0235	0.0292	0.0326	0.0493	0.0493	0.0587	0.0559	0.0588	0.0544
70 (21.1)	0.0199	0.0250	0.0280	0.0431	0.0434	0.0522	0.0503	0.0540	0.0503
80 (26.7)	0.0171	0.0215	0.0244	0.0377	0.0385	0.0467	0.0454	0.0493	0.0467
90 (32.2)	0.0147	0.0188	0.0214	0.0332	0.0341	0.0419	0.0412	0.0451	0.0432
100 (37.8)	0.0128	0.0164	0.0188	0.0294	0.0307	0.0377	0.0375	0.0414	0.0400
110 (43.3)	0.0112	0.0145	0.0167	0.0264	0.0276	0.0342	0.0342	0.0380	0.0370
120 (48.9)	0.0099	0.0128	0.0149	0.0237	0.0249	0.0312	0.0313	0.0352	0.0344
130 (54.4)	0.0088	0.0115	0.0134	0.0226	0.0214	0.0285	0.0288	0.0326	0.0321
140 (60.0)	0.0079	0.0103	0.0121	0.0207	0.0194	0.0262	0.0266	0.0303	0.0300

^A Correction = (mole % C5 in gas) × (glycol circulation, gph) × CF .

^B If pentanes mole % is not known, use 0.80 %.

TABLE X1.6 Hexanes + (C6 +) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0516	0.0614	0.0652	0.1012	0.0962	0.1160	0.1034	0.1079	0.0940
50 (10.0)	0.0419	0.0505	0.0541	0.0850	0.0821	0.1004	0.0909	0.0968	0.0859
60 (15.6)	0.0344	0.0418	0.0454	0.0720	0.0704	0.0872	0.0811	0.0868	0.0783
70 (21.1)	0.0285	0.0349	0.0384	0.0616	0.0609	0.0764	0.0718	0.0787	0.0713
80 (26.7)	0.0239	0.0295	0.0327	0.0530	0.0529	0.0671	0.0639	0.0708	0.0656
90 (32.2)	0.0202	0.0251	0.0280	0.0459	0.0463	0.0592	0.0569	0.0638	0.0599
100 (37.8)	0.0172	0.0215	0.0243	0.0400	0.0407	0.0526	0.0510	0.0578	0.0547
110 (43.3)	0.0147	0.0186	0.0211	0.0351	0.0360	0.0469	0.0460	0.0525	0.0501
120 (48.9)	0.0127	0.0162	0.0185	0.0310	0.0321	0.0421	0.0415	0.0478	0.0460
130 (54.4)	0.0111	0.0142	0.0163	0.0275	0.0287	0.0379	0.0377	0.0437	0.0424
140 (60.0)	0.0099	0.0125	0.0145	0.0246	0.0258	0.0343	0.0343	0.0401	0.0391

^A Correction = (mole % C6 in gas) × (glycol circulation, gph) × CF .

^B If hexanes plus heavies mole % is not known, use 0.65 %.

TABLE X1.7 Pentane (C3) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0152	0.0208	0.0257	0.0218	0.0237	0.0252	0.0262	0.0274	0.0279
50 (10.0)	0.0141	0.0194	0.0241	0.0202	0.0222	0.0237	0.0248	0.0261	0.0269
60 (15.6)	0.0131	0.0182	0.0227	0.0188	0.0208	0.0224	0.0236	0.0250	0.0259
70 (21.1)	0.0123	0.0171	0.0214	0.0176	0.0195	0.0212	0.0225	0.0240	0.0249
80 (26.7)	0.0116	0.0162	0.0203	0.0165	0.0185	0.0201	0.0215	0.0230	0.0241
90 (32.2)	0.0110	0.0154	0.0194	0.0156	0.0175	0.0191	0.0205	0.0222	0.0232
100 (37.8)	0.0104	0.0146	0.0185	0.0148	0.0167	0.0183	0.0197	0.0213	0.0225
110 (43.3)	0.0099	0.0140	0.0178	0.0140	0.0159	0.0175	0.0189	0.0206	0.0217
120 (48.9)	0.0095	0.0134	0.0171	0.0134	0.0153	0.0168	0.0183	0.0199	0.0211
130 (54.4)	0.0091	0.0129	0.0165	0.0128	0.0146	0.0162	0.0176	0.0192	0.0204
140 (60.0)	0.0088	0.0124	0.0159	0.0123	0.0140	0.0157	0.0170	0.0187	0.0199

^A Correction = (mole % C3 in gas) × (glycol circulation, gph) × CF.

^B If propane mole % is not known, use 4.2 %.

TABLE X1.8 Butane (C4) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0179	0.0293	0.0356	0.0327	0.0345	0.0356	0.0356	0.0363	0.0359
50 (10.0)	0.0158	0.0267	0.0328	0.0300	0.0319	0.0333	0.0337	0.0347	0.0347
60 (15.6)	0.0141	0.0244	0.0303	0.0276	0.0297	0.0312	0.0321	0.0332	0.0335
70 (21.1)	0.0126	0.0226	0.0282	0.0255	0.0277	0.0294	0.0305	0.0320	0.0323
80 (26.7)	0.0114	0.0210	0.0265	0.0238	0.0260	0.0277	0.0290	0.0306	0.0313
90 (32.2)	0.0104	0.0196	0.0249	0.0223	0.0245	0.0263	0.0277	0.0294	0.0303
100 (37.8)	0.0095	0.0184	0.0235	0.0209	0.0231	0.0250	0.0265	0.0283	0.0293
110 (43.3)	0.0088	0.0173	0.0224	0.0197	0.0220	0.0239	0.0254	0.0273	0.0284
120 (48.9)	0.0081	0.0164	0.0213	0.0187	0.0209	0.0229	0.0244	0.0264	0.0276
130 (54.4)	0.0076	0.0157	0.0203	0.0178	0.0200	0.0219	0.0315	0.0255	0.0268
140 (60.0)	0.0072	0.0149	0.0195	0.0170	0.0192	0.0211	0.0227	0.0247	0.0260

^A Correction = (mole % C4 in gas) × (glycol circulation, gph) × CF.

^B If butanes mole % is not known, use 2.1 %.

TABLE X1.9 Pentane (C5) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.0955	0.1178	0.1305	0.1379	0.1362	0.1312	0.1227	0.1240	0.1142
50 (10.0)	0.0802	0.1003	0.1116	0.1190	0.1189	0.1161	0.1095	0.1137	0.1056
60 (15.6)	0.0682	0.0859	0.0973	0.1034	0.1044	0.1033	0.0997	0.1036	0.0977
70 (21.1)	0.0583	0.0745	0.0849	0.0908	0.0924	0.0925	0.0904	0.0958	0.0910
80 (26.7)	0.0507	0.0649	0.0751	0.0801	0.0825	0.0833	0.0823	0.0882	0.0852
90 (32.2)	0.0444	0.0575	0.0668	0.0709	0.0738	0.0754	0.0752	0.0814	0.0794
100 (37.8)	0.0391	0.0510	0.0599	0.0634	0.0669	0.0683	0.0690	0.0753	0.0740
110 (43.3)	0.0348	0.0457	0.0540	0.0572	0.0606	0.0625	0.0635	0.0698	0.0691
120 (48.9)	0.0312	0.0413	0.0490	0.0517	0.0551	0.0575	0.0586	0.0651	0.0649
130 (54.4)	0.0282	0.0375	0.0448	0.0471	0.0505	0.0530	0.0543	0.0608	0.0610
140 (60.0)	0.0258	0.0343	0.0412	0.0432	0.0465	0.0491	0.0506	0.0570	0.0576

^A Correction = (mole % C5 in gas) × (glycol circulation, gph) × CF.

^B If pentanes mole % is not known, use 0.80 %.

TABLE X1.10 Hexanes + (C6 +) Correction Factors (CF) for ARL Total VOC Emissions for Units with Kimray Pump^{A,B}

Contactor Temperature, °F (°C)	Contactor Pressure, psig (KPa)								
	200	300	400	500	600	700	800	900	1000
40 (4.4)	0.2040	0.2434	0.2596	0.2855	0.2720	0.2532	0.2268	0.2407	0.2111
50 (10.0)	0.1662	0.2008	0.2161	0.2402	0.2325	0.2197	0.1997	0.2164	0.1933
60 (15.6)	0.1368	0.1669	0.1823	0.2039	0.1998	0.1191	0.1785	0.1946	0.1767
70 (21.1)	0.1138	0.1401	0.1547	0.1747	0.1732	0.1678	0.1586	0.1768	0.1614
80 (26.7)	0.0956	0.1188	0.1324	0.1506	0.1508	0.1479	0.1414	0.1597	0.1489
90 (32.2)	0.0811	0.1016	0.1142	0.1308	0.1324	0.1309	0.1264	0.1443	0.1363
100 (37.8)	0.0694	0.0876	0.0993	0.1143	0.1167	0.1166	0.1137	0.1310	0.1249
110 (43.3)	0.0599	0.0762	0.0871	0.1006	0.1305	0.1042	0.1027	0.1194	0.1148
120 (48.9)	0.0521	0.0667	0.0768	0.0891	0.0924	0.0938	0.0930	0.1092	0.1058
130 (54.4)	0.0456	0.0589	0.0682	0.0793	0.0829	0.0847	0.0847	0.1001	0.0978
140 (60.0)	0.0408	0.0521	0.0609	0.0710	0.0747	0.0769	0.0774	0.0921	0.0906

^A Correction = (mole % C6 in gas) × (glycol circulation, gph) × CF.

^B If hexanes plus heavies mole % is not known, use 0.65 %.

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