

SAMPLING AND HANDLING OF GASOLINES, DISTILLATE FUELS AND C₃-C₄ FRACTIONS

UOP Method 516-00

SCOPE

This method is for the preparation and cleaning of sample cylinders, and for sampling techniques necessary to obtain an air-free sample of a liquid hydrocarbon. The procedures are applicable to liquefied natural gases, high vapor pressure gasolines, various liquefied petroleum gases, air-unstable gasolines or other liquid hydrocarbon products that require rigorous exclusion of air. Sampling for the analysis of sulfur or other heteroatom compounds in C₃-C₄ fractions requires a special cylinder or a special cylinder preparation. An alternative to the sampling system and procedure is available as “Closed Sampling System”, UOP, PIC. If the sample is to be transported offsite, see *NOTE 1*.

OUTLINE OF METHOD

Cylinder cleaning and sampling techniques are specified to obtain a representative, air-free sample in a suitable container, e.g., a double-valved, stainless steel cylinder. For trace sulfur or other heteroatom compound analysis, a Silcosteel[®] coated cylinder is preferred. When coated cylinders are unavailable or impractical, a conventional cylinder is treated (pickled) to make it more stable to sulfur compounds. The clean, leak-free cylinder is mounted vertically near the sampling point and connected to the plant sample line by steel tubing or pipe. The connecting lines are flushed with the sample. After line flushing, the sample is allowed to flow upward through the cylinder. Several volumes of sample are discarded before closing the valves of the cylinder. The cylinders that are used for collection are constructed to provide safe outage.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Cylinder, C₃-C₄ fractions, type 304 stainless steel, high pressure, 12,400 kPa, gauge (1800 psig) maximum working pressure, one-liter capacity, Whitey, Cat. No. 304L-HDF4-1000, or equivalent. Equip the cylinder with outage tube, Whitey, Cat. No. 304L-DTM4-F4-038, two stainless steel valves, Whitey, Cat. No. SS-16DKM4-F4, and two plugs, Whitey, Cat. No. SS-4-P, or equivalent. Smaller cylinders, such as 500-mL, may be used when large quantities of sample are not required.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Cylinder, C₃-C₄ fractions, Silcosteel coated, for trace sulfur and other applications which require a more inert surface than stainless steel, 1000 mL, Restek, Cat. No. 24275. Equip the cylinder with two Silcosteel coated valves, Restek, Cat. No. 24278, an outage tube, Whitey, Cat. No. 304L-DTM4-F4-038, and two caps, Whitey, Cat. No. SS-4-CP. Ship the outage tube to Restek for Silcosteel coating, Restek, Cat. No. 54852. Caustic materials and strong acids will damage the Silcosteel surface. Samples and cleaning procedures must be caustic and acid free.

Cylinder, gasoline and distillate fuels, type 304 stainless steel, 690 kPa, gauge (100 psig) maximum working pressure, Code No. 2, 28-L (7-gal) capacity, with dip tubes, equipped with 2 stainless steel valves. The cylinder without valves is available from Alloy Products, or equivalent. Valves are available from Whitey, Cat. No. SS-1KF4, or equivalent. The cylinder, as received, will be equipped with a long dip tube; the short dip tube, made from 1/4-inch OD stainless steel, must be fabricated and welded to the valve coupling extending into the cylinder approximately 14 cm. Air-free samples of gasoline or distillate fuel oils to be used for treating, oxidation or corrosion studies are typically taken in this cylinder. **CAUTION:** This cylinder cannot be used for samples having a vapor pressure above 275 kPa, gauge (40 psig) at 21°C (70°F).

Cylinder Sampling Assembly, see Fig. 3, required for sampling gasolines or distillates

Fittings, pressure-rated tubing or pipe made of stainless steel for use as transfer and manifold lines with appropriate valves, tees and unions or couplings of these materials. **CAUTION.** Do not use brass, aluminum or copper pipe, tubing, valves, unions, ferrules, or couplings.

Grounding cable, heavy gauge wire or cable connected to a water pipe or to a rod driven into the ground, according to local codes, having a suitable spring clamp to attach it to the metal cylinder; necessary to prevent explosion due to static electricity.

Oven, gravity convection, capable of maintaining 150°C, Fisher Scientific, Cat. No. 13-247-650G

Pail, polyethylene, 13-L capacity, Fisher Scientific, Cat. No. 03-687-10

Regulator, nitrogen, delivery pressure 345-4480 kPa, gauge (50-650 psig), Matheson, Model No. 2-580, or equivalent

Regulator, nitrogen, two-stage, delivery pressure 28-690 kPa, gauge (4-100 psig), Matheson, Model No. 3104-580, or equivalent

Thermometer, Fisher Scientific, Cat. No. 15-077-2B

Vacuum pump, of sufficient capacity to evacuate the cylinder to the extent that the cleaning solution may be drawn into the cylinder

REAGENTS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Acetone, 99.5% minimum purity, Fisher Scientific, Cat. No. A949SK-4

Ferric chloride, Fisher Scientific, Cat. No. I89-500

Hydrochloric acid, 1:1, Fisher Scientific, Cat. No. LC15130-3

Isooctane, 99.5%, low residue, Fisher Scientific, Cat. No. O-301-4

Leak detector, solution, Leak-Check, Alltech Associates, Cat. No. 2025, or equivalent

Methanol, 99.8% minimum purity, Fisher Scientific, Cat. No. A408SK-4

Methylene chloride, 99.9%, low residue, Fisher Scientific, Cat. No. D151-4

Nitrogen, 99.99% minimum purity

Pentane, 99%, low residue, Fisher Scientific, Cat. No. P399SK-4

Pickling solution. Prepare by dissolving 10 ± 0.1 g of ferric chloride in one liter of 1:1 hydrochloric acid.

Steam, local supply

TAM(toluene-acetone-methanol) solution. To prepare, mix equal portions of toluene, acetone and methanol.

TI(toluene-isooctane) solution. To prepare, mix equal portions of toluene and isooctane.

Toluene, 99.8% minimum purity, Fisher Scientific, Cat. No. T290SK-4

Water, deionized or distilled

Water, tap, hot

PREPARATION OF APPARATUS

Cleaning and Drying Cylinders

Proper preparation and cleaning of sample cylinders is of paramount importance. In no case may an improperly cleaned cylinder be used as a sample container. Clean and prepare cylinders as described.

Cylinders for C₃-C₄ Fractions

A. Silcosteel Coated Stainless Steel, or Conventional Stainless Steel if No Sulfur or Other Heteroatom Analysis Is Required

1. Completely empty the cylinder of any residual material in a well ventilated area or fume hood.
2. If the cylinder contained aqueous material, partially fill the cylinder with deionized or distilled water, agitate and drain. Follow the same procedure with methanol.
 - Dispose of all used cleaning solutions in an environmentally safe manner.
3. Partially fill the cylinder (about 1/4) with TI solution, agitate and drain. Follow the same procedure sequentially with pentane, methylene chloride and methanol.

4. Connect one end of the cylinder to a nitrogen source. Connect a length of tubing to the other end to properly vent the cylinder when placed in an oven.
5. Start a flow of nitrogen.
6. Place cylinder in an oven at $\sim 150^{\circ}\text{C}$ and purge with nitrogen for 1 hr.
7. Remove the cylinder from the oven and allow it to cool maintaining a slow flow of nitrogen.
8. Pressure check the cylinder by closing one of the valves and then filling the cylinder with nitrogen to a pressure of approximately 2000 kPa, gauge (290 psig).
9. Close the other valve and disconnect from N_2 line. Completely immerse the nitrogen-pressured cylinder in a bath of clean tap water and observe it for leaks during a 5-minute period.
 - Leaking valves should be repaired or replaced before use.
10. Remove the cylinder from the bath when it is judged to be free of leaks and dry the outside.
11. Release enough nitrogen from the cylinder to retain a pressure of about 260 kPa, gauge (38 psig).
12. Cap or plug the valves to prevent leakage or contamination of the valve connection prior to use.
 - The cylinder is ready for sampling or shipment.

B. Conventional Stainless Steel for Sulfur or Other Heteroatom Containing Sample Analysis

Cylinders that are to be used for samples on which a sulfur analysis is to be performed must be treated with a special “pickling” technique, after they have been cleaned as described above.

1. Connect a 15-cm (6-inch) length of stainless steel tubing to one of the 2 valves on a previously cleaned cylinder.
2. Vent the cylinder, evacuate it for 15 minutes with a vacuum pump and close both valves.
3. Partially open the bottom valve and draw enough pickling solution into the cylinder through the 15-cm length of tubing to equal about one-half the volume of the cylinder.
4. Close the bottom valve and remove the length of tubing from the cylinder.
5. Open the top valve and immerse the cylinder vertically in a pail of tap water at $54\text{--}60^{\circ}\text{C}$ ($130\text{--}140^{\circ}\text{F}$) for 30 minutes, leaving the upper valve open. (*CAUTION:* A pressure buildup will occur in the cylinder during the pickling operation if both valves are closed.) Maintain the water temperature at $54\text{--}60^{\circ}\text{C}$ by occasionally adding hot tap water.
6. Close the upper valve, invert the cylinder, open the other valve and allow the cylinder to soak for another 30-minute period at $54\text{--}60^{\circ}\text{C}$.
7. Remove the cylinder from the hot water bath and drain the pickling solution from the cylinder by opening both valves. Do not reuse the pickling solution.
 - Dispose of all used cleaning solutions in an environmentally safe manner.

8. Flush the cylinder for approximately 1/2 hour with hot tap water and drain as completely as possible.
9. Rinse with deionized or distilled water.
10. Place the cylinder in an oven at ~150°C with both valves open for approximately 30 minutes.
11. Remove the cylinder and purge with nitrogen for 30 minutes or until cool.
12. Pressure check and prepare the cylinder for sampling as previously described in Steps 8 - 12, *Silcosteel Coated Stainless Steel, or Conventional Stainless Steel if No Sulfur or Other Heteroatom Analysis Is Required.*

Cylinders (28-L) for Gasolines and Distillate Fuels

1. Remove the valve fitting connected to the short dip-tube.
2. Empty the cylinder of any residual material in a well ventilated area or fume hood.
3. Introduce steam into the cylinder through the valve on the long dip-tube and allow steam to flow through the cylinder for a period of approximately 24 hours.
4. Shut off the steam and allow the cylinder to cool.
5. Drain as much water as possible through the short dip-tube opening.
6. Add approximately one liter of TAM solution through the short dip-tube opening and replace the valve fitting.
7. Agitate or roll the cylinder for several minutes.
8. Remove the valve fitting and drain the solvent through the short dip-tube opening.
9. Add approximately one liter of acetone to the cylinder through the short dip-tube opening.
10. Agitate, drain and repeat with a second acetone wash.
11. Wash the cylinder with one liter of methanol.
12. Drain as much methanol from the cylinder as possible.
13. Blow dry with nitrogen for three to five minutes to remove all traces of methanol.
14. Install the valve fitting connected to the short dip-tube and flush the cylinder with nitrogen for 10 minutes to remove residual air or solvent.
15. Pressure the cylinder to 260 kPa, gauge (38 psig) using nitrogen.
16. Check for leaks with a leak detector solution.
17. Allow the cylinder to stand overnight and check if a pressure drop has occurred.
18. Confirm the absence of leaks.
19. Cap or plug the valves to prevent contamination of the valve connection prior to use.

PROCEDURE

Selection and Arrangement of Sampling Connections

The sampling line tap should, preferably, extend into the plant transfer line, whether vertical or horizontal, so that the sample will be drawn from the center of the stream. The sampling line should be as short as possible.

Construct a sampling manifold assembly as shown in Fig. 1 when C₃-C₄ fractions are to be sampled. The cylinder sampling manifold is of small-diameter stainless steel pipe or tubing, as compact as possible, and is mounted at the sample tap in a vertical position, as shown in the illustration. *Do not* use aluminum, copper or brass tubing, pipe, valves, unions or couplings in the sampling system assembly.

Arrange the cylinder to be used for sampling of gasoline and distillate fuels as shown in Fig. 2, utilizing the cylinder sampling assembly (Fig. 3) that is shipped with the cylinder. Every effort should be made to tap the plant transfer line at a point where the product temperature is less than 38°C (100°F), and the pressure is less than 310 kPa, gauge (45 psig).

Sampling

General

It is best to obtain the sample from a vertical line as shown in the illustrations. If the sample must be taken from a horizontal line, modify the sampling manifold so that the cylinder will be in a vertical position.

C₃ - C₄ Fractions

The clean, dry cylinder will be received for sampling under about 260 kPa, gauge (38 psig) of nitrogen pressure.

1. Mount the cylinder vertically as illustrated in Fig. 1 with both valves closed and secure it by a brace, K.
2. Connect a grounding cable to the cylinder. *CAUTION:* The grounding cable is necessary to prevent explosion due to static electricity. The grounding cable is connected to a water pipe or to a rod driven into the ground, according to local codes.
3. Attach the manifold assembly to the sample line with a suitable connection, N, and to the sample cylinder with a suitable connection, M.
4. Connect a piece of pipe to cylinder valve, C, with a connector, L, to direct the flow of sample to a suitable stack or exhaust system.
5. Open valve S fully and let P reach the pressure of the plant transfer line.
6. Open A fully. Adjust D to flush the sampling line thoroughly until liquid flows freely through D.
7. Close D and partially open C.
8. Slowly open B. Flush the cylinder with several volumes of sample.

9. Close C, and when the pressure on P is constant, close B.
10. Close S, open D and then close A. Sufficient outage is automatically provided by the short dip tube at valve C.
11. Install plugs or caps in the open ends of the valves and attach an identification tag (see *Identification and Shipment*).

Gasolines and Distillate Fuels

This procedure describes sampling to obtain a large volume (>20-L) air free sample. For smaller volumes (~1-L) use glass bottles, cans or the cylinders described in *Sampling, C₃ - C₄ Fractions*. The clean dry cylinder will be received for sampling under about 260 kPa, gauge (38 psig) of nitrogen pressure.

All necessary fittings, up to and including appropriate fittings on the downstream side of union N, are included as part of the Cylinder Sampling Assembly. A 690 kPa, gauge (100 psig) pressure relief valve is also included as part of the Assembly for automatic emergency relief. Under no circumstances should this valve be removed or any attempt made to defeat its purpose. Under no circumstances should the feed pressure to the cylinder exceed 520 kPa, gauge (75 psig).

1. Close all valves.
2. Connect the Cylinder Sampling Assembly (Fig. 3) as illustrated in Fig. 2. The tee *must* be connected to the *long* dip-tube valve B of the cylinder, identified with the metal tag.
3. Connect a grounding cable to the cylinder. **CAUTION:** The grounding cable is necessary to prevent explosion due to static electricity. The grounding cable is connected to a water pipe or to a rod driven into the ground, according to local codes.
4. Open valves A and B. A positive deflection of the pressure gauge will occur since the cylinder had been pressured to 260 kPa, gauge, prior to shipping.
5. Close valve B and observe the pressure gauge to see if pressure is retained and all fittings are leak-free.
6. Re-open valve B and then partially open valve D until the cylinder pressure decreases to 35 kPa, gauge (5 psig).
7. Close valve B. Flush the sample line by opening first valve D, then valve A and adjusting liquid flow with valve S.
8. Flush for an additional 15 seconds after bubbles no longer exit at valve D.
9. Slowly close valve D while observing the pressure gauge. If the pressure exceeds 240 kPa, gauge (35 psig) before valve D is fully closed, adjust the flow with valve D to obtain 240 kPa, gauge.
10. Open valve B and then slowly open valve C allowing the cylinder to fill with the process liquid.
11. Observe the pressure gauge and adjust valve C to maintain positive pressure on the system. When liquid appears at the exit of valve C, close valve C and allow the system to equilibrate at 240 kPa, gauge (35 psig) or at plant line pressure, whichever is lowest. Sufficient outage is automatically provided by the short dip-tube at valve C.

12. Close valve B and then valve S. Open valve D.
13. Disconnect the Cylinder Sampling Assembly at union N and valve B.
14. Disconnect the waste lines from valves C and D.
15. Flush the Cylinder Sampling Assembly with air or inert gas. If the cylinder pressure is 170-240 kPa, gauge (25-35 psig), sampling is completed and go to Step 21. If the plant transfer line pressure was less than 170 kPa, gauge (25 psig), continue with Step 16.
16. Reconnect the Cylinder Sampling Assembly to valve C as illustrated in Fig. 4.
17. Ground the cylinder. Attach a high purity nitrogen source equipped with an appropriate pressure reducing regulator and regulating valve N at valve A.
18. Flush the Cylinder Sampling Assembly with nitrogen for 3 minutes by opening valves D and A and adjusting the flow with valve N.
19. Loosen the connection at valve C to purge air from the connecting tube and then re-tighten.
20. Set the regulator delivery pressure at 240 kPa, gauge (35 psig), close valve D and open valve C to pressure the sample cylinder to 240 kPa, gauge.
21. Close valves C and then N. Open valve D.
22. Disconnect the Cylinder Sampling Assembly.
23. Install caps on open valve ends, repackage the fittings and cylinder in the shipping crate and attach an identification tag (see *Identification and Shipment*).

Identification and Shipment

1. Identify each sample by attaching a tag to the cylinder giving company name and location, time and date of sampling, identity of stream sampled, sample pressure and tests required. Health, reactivity and flammability must also be noted along with any special PPE requirements for handling.
2. Affix an appropriate shipping label to the crate and include documentation as required by federal, state and local regulations.

NOTES AND PRECAUTIONS

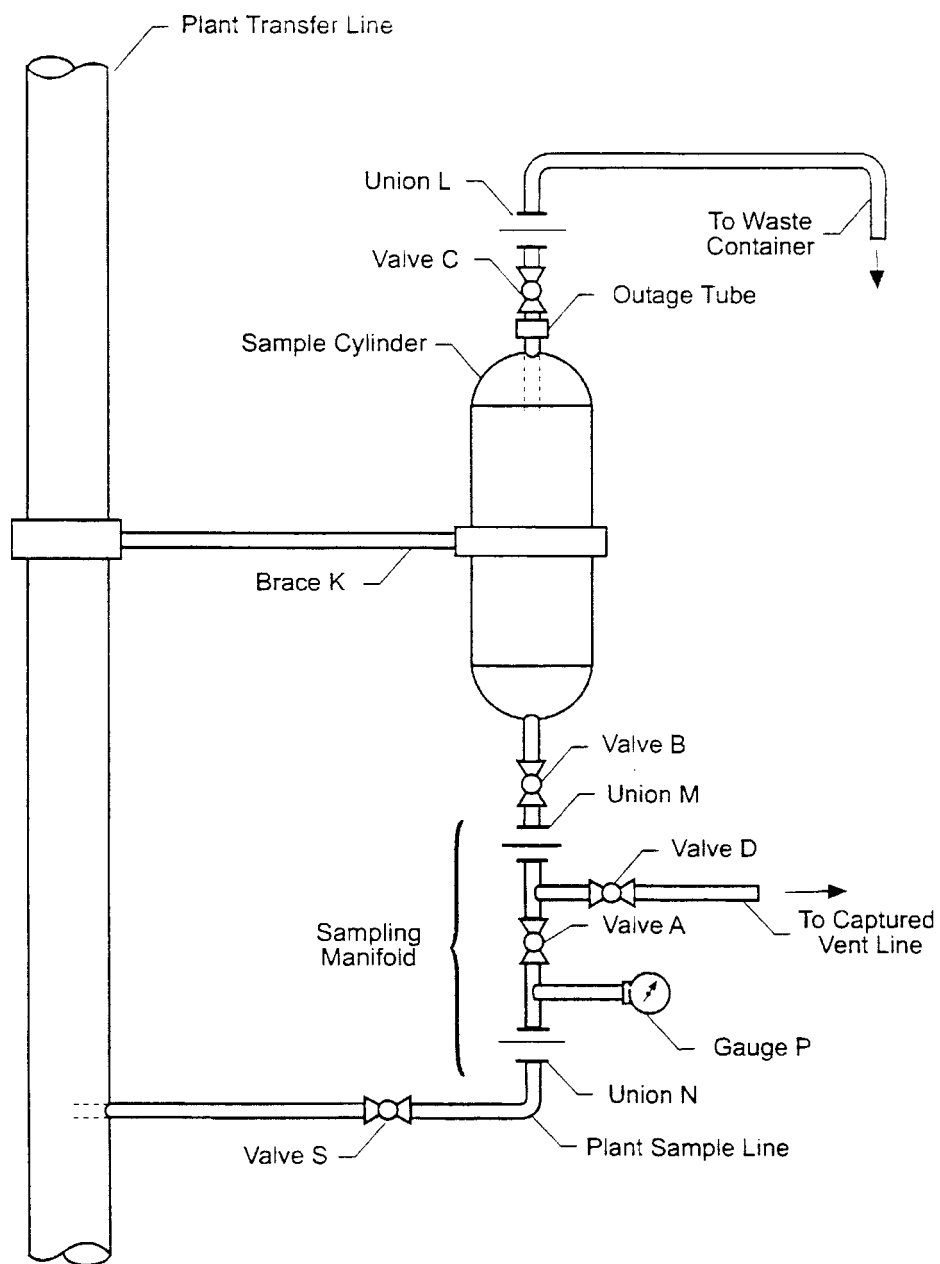
1. If samples are to be transported offsite, follow the regulations of the governments and transportation systems involved. In the United States, these can be found in U. S. DOT Regulations, 49 CFR Transportation, Subtitle B, Parts 171-180, and OSHA Regulations 29 CFR Paragraphs 1910.1000 and 1910.2000. For example, DOT regulations specify that sample vapor pressure is not to exceed 275 kPa gauge (40 psig) at 21°C (70°F) for shipment of cylinders containing gasolines or distillates.
2. Samples taken in containers found leaking either during or after sampling should be discarded and new samples taken in leak-free cylinders.

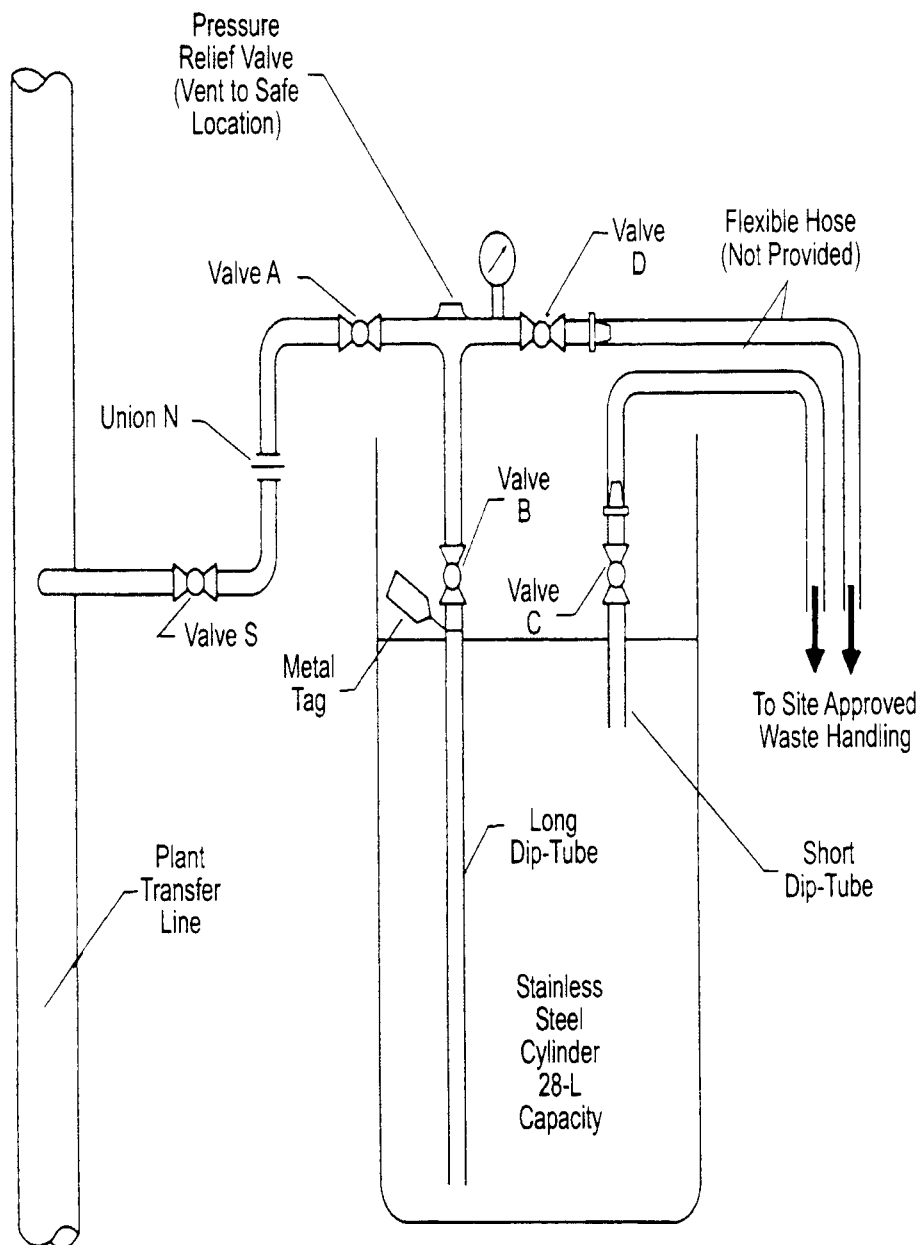
REFERENCES

- U. S. DOT Regulations, 49 CFR Transportation, Subtitle B, Parts 171-180, Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402
- U. S. OSHA Regulations 29 CFR Paragraphs 1910.1000 and 1910.2000, Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402

SUGGESTED SUPPLIERS

- Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
www.alltechweb.com
- Alloy Products Corp., 1045 Perkins Ave., Waukesha, WI 53187 (262-542-6603)
www.alloyproductscorp.com
- Fisher Scientific, 50 Fadem Rd., Springfield, NJ 07081-3193 (973-467-6400) www.fishersci.com
- Matheson Gas Products, Inc., 932 Paterson Plank Road, East Rutherford, NJ 07073 (201-933-2400)
www.mathesontrigas.com
- Restek Corp., 110 Benner Circle, Bellefonte, PA 16823 (814-353-1300) www.restekcorp.com
- UOP, PIC (Process Information and Control), 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (847-391-2529) www.uop.com
- Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143 (440-473-1050) www.swagelok.com

**Figure 1**Sampling of C₃-C₄ Fractions

**Figure 2**

Sampling Gasoline
and Distillate Fuels

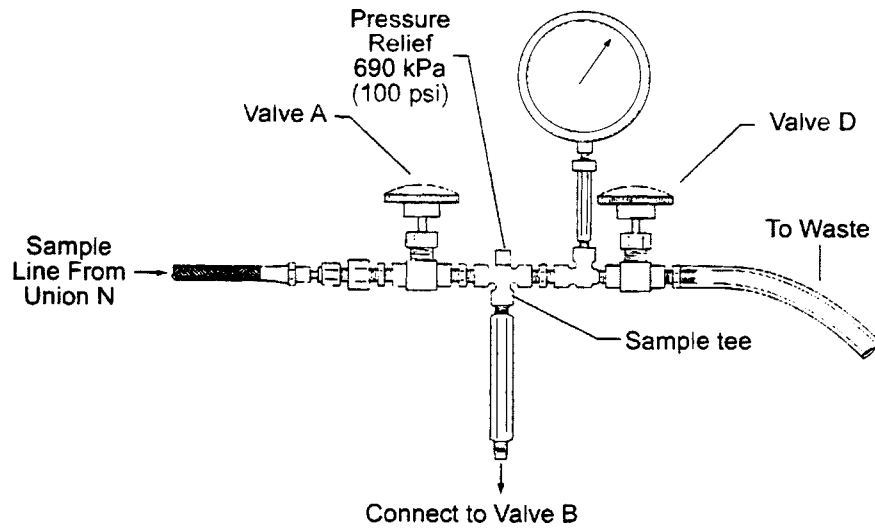


Figure 3

Cylinder Sampling Assembly

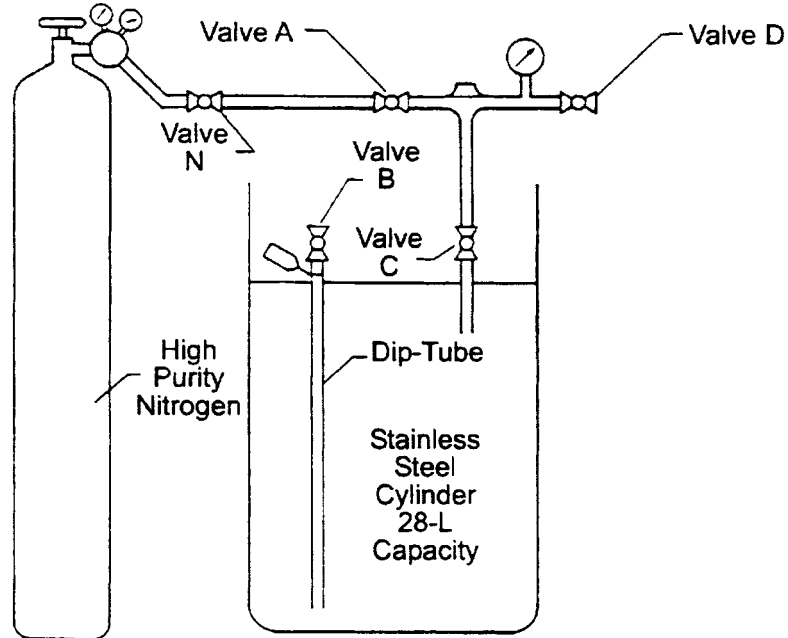


Figure 4

Sample Pressuring System