

California Environmental Protection Agency



Vapor Recovery Test Procedure

PROPOSED: TP-201.2H

Determination of Hazardous Air Pollutants from
Vapor Recovery Processors

Adopted: _____

All text is proposed for adoption.

**California Environmental Protection Agency
Air Resources Board**

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**Determination of Hazardous Air Pollutants from
Vapor Recovery Processors**

Definitions common to all certification and test procedures are in:

D-200 Definitions for Vapor Recovery Procedures

For the purpose of this procedure, the term "CARB" refers to the State of California Air Resources Board, and the term "Executive Officer" refers to the CARB Executive Officer, or his or her authorized representative or designate.

1. PURPOSE AND APPLICABILITY

Sample collections are to be performed by, or under supervision of, persons who are experienced in the performance of the source sampling procedures required by this method. Sample analyses are to be performed by, or under supervision of, persons who are experienced in the performance of the analytical procedures required by this method. Particular care should be exercised in the area of safety concerning the choice of equipment and operation in potentially explosive or flammable atmospheres.

- 1.1 The purpose of this test procedure is to determine mass emissions of carbonyls (aldehydes and ketones), benzene, and 1,3 butadiene in the exhaust gas from gasoline vapor recovery system combustion processors at gasoline stations.
- 1.2 This procedure is applicable to combustion devices in general. Although the procedure is written to reflect application to gases associated with gasoline vapor recovery combustion devices, it need not be limited to gasoline vapor recovery systems.

2. PRINCIPLE AND SUMMARY OF TEST PROCEDURE

Determination of mass emission rates of carbonyls, benzene, and 1,3 butadiene requires the calculation of the processor exhaust flow rate and the concentrations of the target compounds in the exhaust.

2.1 Flow Rate

Processor exhaust flow rate is determined by measuring inlet flow and then adjusting it with a dilution value based on the amount of carbon entering and leaving the processor (carbon balance). Carbon balance determinations require measurements

of inlet total hydrocarbons and outlet total hydrocarbons, carbon dioxide, and carbon monoxide. Oxides of nitrogen (NO_x) concentrations must be monitored for possible interference in determining 1,3 butadiene.

2.2 Hazardous Air Pollutants Concentrations

Concentrations of 1,3 butadiene and benzene are determined by GC/FID or GC/PID either directly or after sample collection in Tedlar bags or Summa-polished canisters. Concentrations of carbonyls are determined by HPLC after sample collection in acidified 2,4-dinitrophenylhydrazine (DNPH)-absorbing solution in impingers or DNPH-impregnated cartridges. The flow rates are measured concurrently with the sample collection. Additional selective ion analysis by GC/MS may be required to resolve co-eluting peaks. The DNPH solution, Tedlar bags, and canisters are analyzed on-site or in a laboratory as soon as possible but no later than 72 hours after collection. Analysis for 1,3 butadiene concentrations must be by direct sampling into the appropriate analytical instrument if oxides of nitrogen concentration is unknown or exceeds 5 ppm or collected stack gases are acidic (pH <4).

Benzene and 1,3 butadiene analysis includes cryotrapping a desired gas sample. The trapped sample is thermally desorbed into a gas chromatograph system with a flame ionization detector (GC/FID) or photoionization detector (GC/PID).

Separate analyses may be required for benzene and 1,3 butadiene. Separate collection and analysis is required for carbonyls.

3. BIASES AND INTERFERENCES

- 3.1** Oxides of nitrogen (NO_x) concentrations greater than 5 ppm are expected to reduce 1,3 butadiene concentrations in the sample container.
- 3.2** Any compound with the same retention time as the target compounds is a potential interference.
- 3.3** Samples collected too close to the combustion zone can result in unrepresentative concentrations.
- 3.4** Gases absorbed in particulate matter will not be included in the results. And, particulate matter-trapped gases desorbed into the sample stream will be included. Neither bias situation has been investigated.
- 3.5** Concentrations of 1,3 butadiene could be lowered if the collected stack gas pH is less than 4 (acidic) and the sample is not analyzed directly from the sample line.
- 3.6** Water condensed in the sample lines or sample containers may result in lowered benzene and 1,3 butadiene concentrations.
- 3.7** Sunlight can degrade samples. Sample must be protected from light during sampling, transportation, storage, and analysis.

- 3.8** Full sample bags indicate the sample was collected over a time period less than desired or required. Bags shall be less than 80% full and less than 50% if they travel by air.

4. SENSITIVITY, RANGE, AND PRECISION

4.1 Range and Sensitivity

Concentration ranges for grab samples of benzene and 1,3 butadiene are 20 to 10,000 parts per billion carbon (ppbC) per ARB Methods 1002 (Determination of C₂ to C₅ Hydrocarbons in Automotive Source Samples by Gas Chromatography) and 1003 (Determination of C₆ to C₁₂ Hydrocarbons in Automotive Source Samples by Gas Chromatography). And, 1 to 100 ppb with 10 per cent sensitivity for direct measurement of 1,3 butadiene per ARB Test Method 422 (Determination of Volatile Organic Compounds in Emissions from Stationary Sources). Carbonyl masses range between 0.02 and 200 ug per ARB Method 1004 (Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography). Range and sensitivity for other parameters are the same as for TP-201.2 (Determination of Efficiency of Phase II Vapor Recovery Systems for Dispensing Facilities) or CARB Test Method 100 (Procedures for Continuous Gaseous Emission Stack Sampling).

4.2 Precision

The precision of this method has not yet been determined.

5. EQUIPMENT

Use of trade or manufacturer's names are not a recommendation nor endorsement by the ARB. These names are used as examples of equipment that should meet or exceed the required specifications.

5.1 Flow Measurement

- 5.1.1 Volume Meter, Barometer, Temperature Monitor, and Stopwatch.** Use volume meter and supporting equipment described in US EPA Method 2A or CARB Test Procedure TP-201.2.
- 5.1.2 Hydrocarbon Analyzers (2).** Use hydrocarbon analyzers and supporting equipment described in US EPA Test Method 25A or 25B or CARB Test Procedure TP-201.2. An NDIR HC analyzer is recommended for inlet measurements. An FID HC analyzer is recommended for exhaust measurements.
- 5.1.3 CO Analyzer.** Use a CO analyzer and supporting equipment described in US EPA or CARB Test Method 10, CARB Test Procedure TP-201.2, or CARB Test Method 100.

- 5.1.4 CO₂ Analyzer.** Use CO₂ analyzer and supporting equipment described in US EPA Test Method 3A, CARB Test Procedure TP-201.2, or CARB Test Method 100.
- 5.1.5 NO_x Analyzer.** Use NO_x analyzer and supporting equipment described in CARB Test Method 100 or US EPA Test Method 7E.

5.2 Benzene and 1,3 Butadiene Sampling

- 5.2.1 Tedlar® Sampling Bags or Summa-Polished Canisters.** Tedlar sampling bags must meet or exceed specifications in CARB Test Method 422. Use at least three (3) sample bags for stack samples plus one (1) bag for ambient sample. Use additional bags or canisters as required by ARB Method 422, 1002, and 1003 for blanks, spikes, and collocated samples. Bags and canisters are to be leak-checked, purged, cleaned, and contamination checked by the analytical laboratory. Canisters are also to be evacuated by the analytical laboratory
- 5.2.2 Sample Probe.** Use quartz, borosilicate glass, or Teflon®-lined stainless steel tubing to draw the sample from the stack. Teflon® should not be used in locations above 750° F. Probe should be long enough to traverse stack and at the the same time avoid injury to the probe handler.
- 5.2.3 Sample line.** Use up to 10 feet of unused Teflon® sample line. Sample line should have adapters at each end for leak-tight connections to the sample probe and Tedlar bags. Sample lines longer than 10 feet must be insulated and heated to 225 – 275 degrees Fahrenheit during sample collection.
- 5.2.4 Vacuum Pump.** Use a vacuum pump and sufficient supporting equipment per CARB Test Method 422 to purge the sample line and probe prior to collecting samples and evacuate the bag sampler for sample collection.
- 5.2.5 Bag Sampler.** Use a rigid container bag sampler and supporting equipment described in CARB Test Method 422. Bag sampler is not necessary with Summa-polished canisters. Only sample probe, line and bag or canister assembly must be leak-tight.
- 5.2.6 pH Indicator.** Must be able to indicate a stack gas pH of 4 or higher in accordance with CARB Test method 422.
- 5.2.7 Portable GC.** Use a portable gas chromatography instrument such as Photovac GC as specified by ARB Test method 422 for 1,3 butadiene analysis directly from the sample line.

5.3 Carbonyls

Use sampling and support equipment described in CARB Test Method 430.

6. CALIBRATIONS

All measuring device(s) shall be calibrated in accordance with acceptable procedures. Refer to the appropriate test method(s) in Section 5 above for acceptable calibration procedures.

7. PRE-SAMPLING PROCEDURES

- 7.1** Locate inlet and outlet sampling and monitoring locations in accordance with US EPA Method 2B or CARB Method TP-201.2. Check stack temperature during a burn cycle at the outlet sampling location. Temperatures above 750 °F may indicate outlet sampling location is too near the combustion zone. Relocate outlet sampling location as necessary – use a stack extension if necessary.
- 7.2** Assemble, install, and leak check flow monitoring equipment (including analyzers sampling system) in accordance with US EPA Method 2B or CARB Test Procedure TP-201.2.
- 7.3** Assemble, install, and leak check NO_x analyzers in accordance with CARB Test Method 100 or US EPA Method 7E.
- 7.4** Assemble bag or canister grab sampling system in accordance with CARB Test Method 422. During one or more of the observed burns, purge the sampling line and probe with stack gases using the vacuum pump. Purge the sampling probe and lines with a volume of stack gas equal to at least three (3) volumes of the sample line and probe. Leak check sampling probe, line, and sample bag, or canister. (If NO_x is measured and less than 5 ppm and stack gas acidity is measured at pH 4 or higher, 1,3 butadiene analysis may be made from the grab sample.)
- 7.5** Assemble 1,3 butadiene direct sampling and analysis system in accordance with CARB Test Method 422. Direct sampling and analysis for 1,3 butadiene is required if NO_x concentrations are unknown or greater than 5 ppm, or stack gas pH is less than 4.
- 7.6** Prepare DPNH and assemble carbonyl sampling system in accordance with CARB Test Method 430.
- 7.7** Product dispensing (vehicle fueling) may occur during sampling. There shall be no Phase I deliveries into or out of the gasoline storage tanks connected to the combustion processor within 3 hours prior or during carbonyl, 1,3 butadiene, and benzene sampling.

8. SAMPLING PROCEDURE

- 8.1** Check stack temperature, set up flow equipment, and confirm monitoring equipment is operating correctly during one or more observed burns.
- 8.2** Prior to sample burn, operate flow monitoring equipment, including CO, CO₂, and THC analyzers, in accordance with US EPA Method 2B or CARB method TP-201.2.

- 8.3** Operate NOx analyzer with the analyzers mentioned in Section 8.2 above in accordance with CARB Test method 100 or US EPA Test Method 7E.
- 8.4** Traverse the stack with the continuous emission monitors (CEM) sampling probe. Use the CEM results to locate CEM, benzene, and 1,3 butadiene sampling locations based on an average stack of the measured stack gas concentrations.
- 8.5** Inspect the Tedlar bags or Summa-polished canisters. Remove excess gas from bags or check canister vacuum. Connect Tedlar bag or Summa-polished canister to the sample line. Complete any initial label recordings.
- 8.6** Record initial readings of volume meter, gasoline dispensing totalizer(s) and mark analyzer strip charts and/or dataloggers in a manner consistent with TP-201.2 prior to sample collection.
- 8.7** Insert 1,3 butadiene and benzene sampling probe(s) into the stack and begin evacuating the rigid bag sampling container. At the start of the next burn (indicated by rising stack temperature), open the bag or canister flow control valve and collect the sample in accordance with CARB Test Method 422 sampling procedures.
- 8.7.1** If the burn stops before the sample is collected, close the flow control valve immediately at the end of the burn. Reopen the valve at the start of the next burn. Continue opening and closing the valve with the burn cycles until the sample(s) is collected.
- 8.7.2** After the Tedlar bag is full enough or there is no more vacuum in the Summa-polished canister, close the flow control valve and sample bag or canister valve.
- 8.7.3** Disconnect the bag sample from the sampling line. Complete the sample label. Transfer required information to the chain of custody log.
- 8.8** Insert carbonyl sampling probe into the stack and collect a sample in a manner consistent with Sections 8.7 through 8.7.3 above.
- 8.9** After sample collection, mark strip charts and record final meter and totalizer readings for the collected sample in a manner consistent with TP-201.2 and CARB Test Method 100.
- 8.10** Repeat the grab sampling cycle for the second, third, and any additional carbonyl, 1,3 butadiene, or benzene samples. Do not collect samples at a rate greater than one carbonyl, 1,3 butadiene, and benzene sample per burn. If necessary, use more than one bag or canister for a complete sample.
- 8.11** Immediately after collecting a set of stack samples for carbonyl, 1,3 butadiene, and benzene, collect ambient air samples for carbonyl, 1,3 butadiene, and benzene. If direct sampling and analysis is used for 1,3 butadiene, the same set up should be used to analyze ambient air. The ambient sample is used to determine background concentrations of the target compounds.

- 8.11.1 Select an ambient air location near the processor but upwind of it, the gasoline dispensers, and other possible gasoline vapor vents.
- 8.11.2 Holding the probe straight up in the air with the sampling end 8 feet or higher above ground.
- 8.11.3 Purge the sample line in a manner consistent with the purge for the stack samples. Purge volume should be near the same as purge volume for the stack samples.
- 8.11.4 Connect the ambient sample Tedlar bag, Summa-polished canister, or carbonyl sample train to the sample line as appropriate for the ambient sample to be collected. Connect the direct sampling and analysis system if this method is used to determine 1,3 butadiene stack gas concentrations.
- 8.11.5 With the probe still in the air, open the sample flow control valve.
- 8.11.6 When the sample is collected, close the valve and disconnect from the sample line.
- 8.11.7 If another stack sample is to be collected after the ambient sample, purge the sample probe and sample line with stack gas as required above.

9. POST-SAMPLING PROCEDURES

Protect bag samples from light. Transport sample Tedlar bags or Summa-polished canisters in accordance with CARB Test Method 422 for analysis as soon as possible. Analyze grab samples within 72 hours of collection.

10. ANALYTICAL PROCEDURES

10.1 Benzene Analysis

Follow CARB Method 1002 or 1003 for sample recovery, analytical materials, and analytical procedures for benzene analysis.

10.2 1,3 Butadiene Analysis

10.2.1 Direct Sample Analysis. Collect and analyze sample directly from stack with portable Photovac GC in accordance with CARB Test Method 422.

10.2.2 Grab Samples. If NO_x and acidic requirements specified in Section 7.5 above allow grab sampling, follow CARB Test Method 1002 for sample recovery, analytical materials, and analytical procedures for 1,3 butadiene analysis.

10.3 Carbonyl Analysis

Follow CARB Method 1004 for sample recovery, analytical materials, and analytical procedures for benzene analysis.

11. QUALITY ASSURANCE/QUALITY CONTROL

11.1 Flow Determination

Follow QA/QC requirements, as appropriate, in CARB Test Procedure TP-201.2, CARB Test Method 100, and US EPA Test Method 2A, 3A, 7E, 10, 25A, and 25B.

11.2 Bag Sampling

Follow sampling QA/QC procedures in CARB Test Method 422.

11.3 Carbonyls Sampling

Follow sampling QA/QC procedures in CARB Test Method 430.

11.4 Sample Analysis

11.4.1 Benzene. Follow the analytical QA/QC in CARB Method 1002 or 1003.

11.4.2 1,3 Butadiene

11.4.2.1 Direct Sampling. Follow the analytical QA/QC in CARB Test Method 422 for direct sampling by portable Photovac GC.

11.4.2.2 Grab Sampling. Follow the analytical QA/QC in CARB Test Method 1002.

11.4.3 Carbonyls. Follow the analytical QA/QC in CARB Method 1004.

12. CALCULATING RESULTS

During calculations retain at least one decimal figure beyond that of the acquired data. Round off results to the proper decimal figure after the final calculation.

12.1 Concentrations

Determine mean concentrations of inlet hydrocarbons, outlet CO₂, outlet CO, outlet NO_x and outlet hydrocarbons according to the procedures in the respective methods and the analyzers' calibration curves, and for the time intervals specified. Concentrations should be determined on a parts per million by volume (ppm) basis.

12.2 Volume Standardization

Standard conditions are 68°F (528°R) and 29.92 in. Hg.

Directly measured volumes (such as inlet volume to combustion processor) shall be standardized as follows before using in other calculations:

$$V_{is} = V_m (528/T) * \{[P_b + (P/13.6)] / 29.92\}$$

where:

- V_{is} = inlet volume corrected to standard conditions (ft³).
- V_m = measured inlet volume (ft³).
- P_b = barometric pressure (in. Hg).
- P = differential pressure at volume meter (in. water, gauge).
- T = temperature of gas stream (°R).

12.3 Exhaust Gas Volume

Calculate the exhaust gas volume as follows:

$$V_{es} = V_{is} \frac{K (HC_i)}{K(HC_e) + CO_{2e} + CO_e - 300}$$

where:

- CO_e = Mean carbon monoxide concentration in system exhaust, ppm.
- CO_{2e} = Mean carbon dioxide concentration in system exhaust, ppm.
- HC_e = Mean hydrocarbon concentration in system exhaust as defined by the calibration gas, ppm.
- HC_i = Mean hydrocarbon concentration in system inlet as defined by the calibration gas, ppm. (1% = 10,000 ppm)
- $.K$ = Calibration gas factor (number of carbon atoms cal. gas molecule)
 - = 2 for ethane calibration gas.
 - = 3 for propane calibration gas.
 - = 4 for butane calibration gas.
 - = Appropriate response factor for other calibration gas.
- s = Corrected to Standard Conditions, 68°F and 29.92 in. Hg.
- V_{es} = Exhaust gas volume, ft³
- V_{is} = Inlet gas volume, ft³.
- 300 = Estimated concentration of ambient CO₂, ppm. (CO₂ concentration in the ambient air may be measured during the test period using an NDIR).

12.4 Exhaust Gas Volume Flow Rate.

Calculate the exhaust gas volume flow rate as follows:

$$Q_{es} = V_{es} / t$$

where:

- Q_{es} = Exhaust gas volume flow rate at standard conditions, ft³/min.
- V_{es} = Exhaust gas volume corrected to standard conditions, ft³.

t = Volume run time for V_{es} , min.

12.5 Mass Emission Rate

Calculate the mass emission rate as follows:

$$m = MW * (C/385) * Q_{es}$$

where:

- m = mass emissions, lb/min.
- MW = Molecular weight of compound (if measured directly) or calibration gas (if measured indirectly), lb/lb-mole.
- C = Concentration of compound of interest, decimal fraction (1.00 = 100% = 10^6 ppm).
- 385 = Gas volume for lb-mole at standard conditions, $ft^3/lb-mole$.
- Q_{es} = Gas volume flow rate, ft^3/min .

13. REPORTING RESULTS

Report all results necessary for making any and all calculations specified in Section 10, "Calculating Results," above. Include laboratory sample modifications (including sample dilution) and analytical results.

14. ALTERNATIVE TEST PROCEDURES

Test procedures, other than specified above, shall only be used if prior written approval is obtained from the ARB Executive Officer. In order to secure the ARB Executive Officer's approval of an alternative test procedure, the applicant is responsible for demonstrating to the ARB Executive Officer's satisfaction that the alternative test procedure is equivalent to this test procedure.

14.1 Such approval shall be granted on a case-by-case basis only. Because of the evolving nature of technology and procedures for vapor recovery systems, such approval shall not be granted in subsequent cases without a new request for approval and a new demonstration of equivalency. Approvals may also require acceptance by local jurisdictions (local APCD or AQMD).

14.2 Documentation of any such approvals and demonstrations shall be maintained in the ARB Executive Officer's files and shall be made available upon request. The tester should also maintain a file of any such approvals and acceptances, and make them available, as necessary, in any affected test report.

15. REFERENCES

15.1 Copies of US EPA test methods mentioned in this test procedure may be obtained from 40 CFR Part 60 Appendix A.

15.2 Copies of ARB test methods or procedures mentioned in this test procedure may be obtained from 17 CCR Part III, Chapter 1, Subchapter 8, Articles 1 & 2.

16. FIGURES

16.1 Example of Tedlar Bag Sampling Set Up with Direct Sampling by Photovac Portable GC.

16.2 Example of Summa-polished Canister Sampling Set Up with Direct Sampling by Photovac Portable GC.

Figure 16-1

Example of Bag Sampling Set Up with
Photovac GC Direct Sampling Set Up

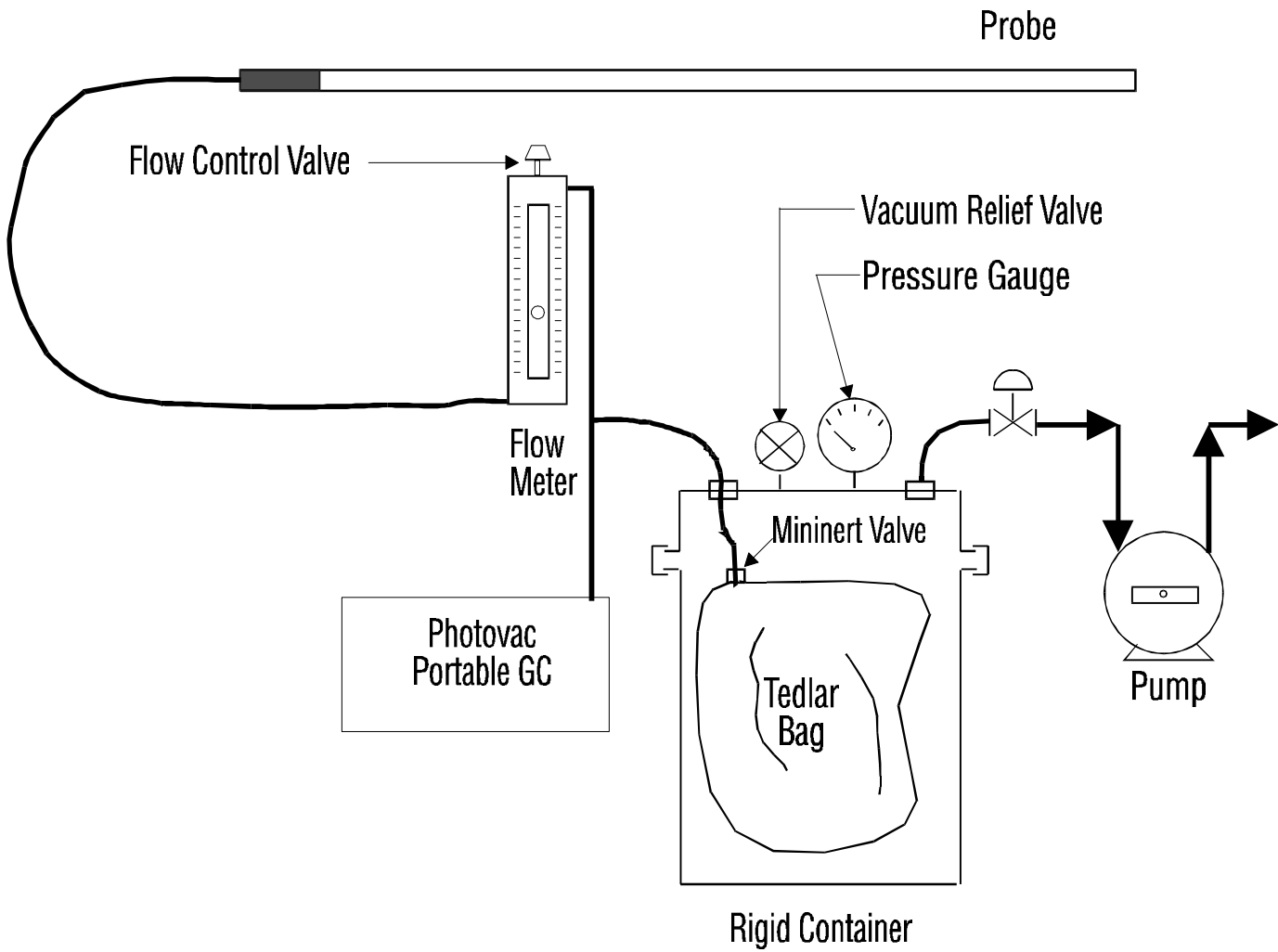


Figure 16-2

**Example of Summa-Polished Canister
Sampling Set Up with
Photovac GC Direct Sampling Set Up**

