Designation: D 6060 – 96

Standard Practice for Sampling of Process Vents With a Portable Gas Chromatograph[1]

This standard is issued under the fixed designation D 6060; 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.

1. Scope

1.1 This practice describes a method for direct sampling and analysis of process vents for volatile organic compound (VOC) vapors and permanent gases using a portable gas chromatograph (GC).

1.2 This practice is applicable to analysis of permanent gases such as oxygen (O_2), carbon dioxide (CO_2) and nitrogen (N_2), as well as vapors from organic compounds with boiling points up to 125°C.

1.3 The detection limits obtained will depend on the portable gas chromatograph and detector used. Detectors available include thermal conductivity, photoionization, argon ionization, and electron capture. For instruments equipped with thermal conductivity detectors, typical detection limits are one to two parts per million by volume (ppm(v)) with an applicable concentration range to high percent by volume levels. For instruments with photoionization detectors detection limit of one to ten parts per billion by volume (ppb(v)) are obtainable with a concentration range from 1000 to 2000 ppm(v). The argon ionization detector has an achievable detection limit of one (ppb(v)), while the electron capture detector has an achievable detection limit of one part per trillion by volume (ppt(v)) for chlorinated compounds.

1.4 The applicability of this practice should be evaluated for each VOC by determining stability, reproducibility, and linearity.

1.5 The appropriate concentration range must also be determined for each VOC, as the range will depend on the vapor pressure of the particular VOC.

1.6 *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.* Refer to Section 8 on Hazards for additional safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]
D 3464 Test Method for Average Velocity in a Duct Using a Thermal Anemometer[2]
D 3154 Test Method for Average Velocity in a Duct (Pitot Tube Method)[2]
E 355 Practice for Gas Chromatography Terms and Relationships[3]

2.2 *Other Document:*

NFPA 496 Standard for Purged and Pressurized Enclosures for Electrical Equipment[4]

3. Terminology

3.1 *Definitions*—For the definition of terms used in this practice, refer to Terminology D 1356 and Practice E 355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *portable*—refers to gas chromatograph with internal battery, internal sample pump, and internal/rechargeable carrier gas supply cylinder.

4. Summary of Practice

4.1 One end of a sampling line (typically 6 mm (¼ in.) outside diameter TFE-fluorocarbon tubing) is connected to a tee in a process vent and the other end to a condensation trap (see 6.1), which is connected to a gas sampling bulb. The outlet of the gas sampling bulb is connected to a sampling pump set at a flow rate of 0.5 to 2 L/min. The sample line from the portable gas chromatograph is inserted through the septum port of the gas sampling bulb. At user selected intervals, the internal pump of the portable gas chromatograph is activated and process vapors drawn through the injection valve of the gas chromatograph and analyzed.

5. Significance and Use

5.1 This practice has been widely used to obtain mass balance data for process scrubbers, to determine the efficiency of VOC emission control equipment, and to obtain data to support air permit applications.

5.2 This practice will have applications to the MACT Rule

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[1] This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from National Fire Protection Assoc., 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

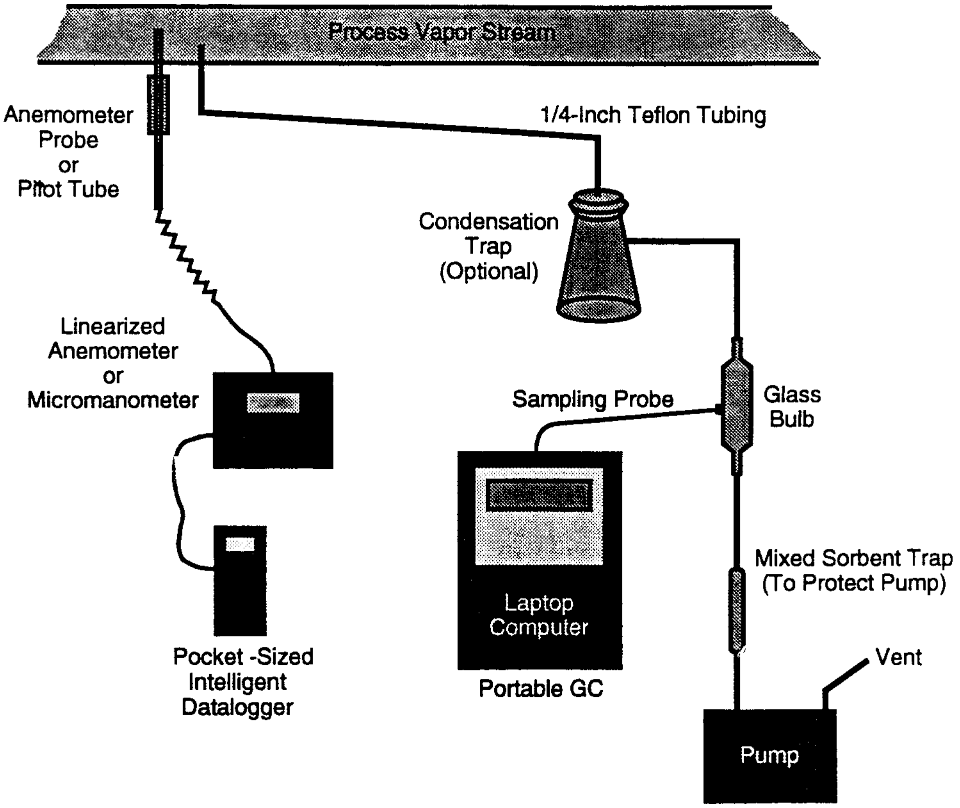

FIG. 1 Schematic of Process Sampling Equipment

and may have applications to Compliance Assurance Monitoring verification required by the 1990 Clean Air Act Title III Amendments.

5.3 This practice, when used with Test Methods D 3464 or D 3154 or on-line process flow meter data, can be used to calculate detailed emission rate profiles for VOCs from process vents.

5.4 This practice provides nearly real time results that can detect process changes or upsets that may be missed using conventional sorbent tube or integrated gas sampling bag sampling.

6. Interferences

6.1 Water or liquid in the process line will plug the sample line of the gas chromatograph, since the injection valve of most portable GCs is not heated. The condensation trap is designed to protect the portable gas chromatograph if liquids are present or occur during process upset.

6.2 Interferences sometimes result from analytes having similar retention times during gas chromatography.

6.3 General approaches which can be followed to resolve such interferences are given below:

6.3.1 Change the type of column, length of column, or operating conditions.

6.3.2 Analyze using a nonpolar methyl silicone column which separates according to boiling point of the compounds and a polar column whose separations are influenced by the polarity of the compounds.[5]

6.3.3 Use a mass spectrometer to verify the identity of peaks.

7. Apparatus

7.1 A schematic drawing of a typical sampling setup is shown in Fig. 1. The laptop computer may be physically located near the gas chromatograph as shown in Fig. 1, or located remotely. In addition, some portable gas chromatographs have an integral computer. Use a short piece of 1.5 mm (1⁄16 in.) outside diameter by 1 mm (0.04 in.) inside diameter stainless steel tubing as the sampling probe line from the gas sampling bulb to the GC inlet.

7.2 *Portable Gas Chromatograph (GC)*, with a thermal conductivity, photoionization, argon ionization, electron capture or appropriate detector, internal/rechargable carrier gas supply, and internal sampling pump.

7.2.1 Portable gas chromatographs are typically equipped with particulate filters which should be replaced periodically.

7.3 *Data Logger*, device used for automated storage of output from a flow measurement device.

7.4 *Gas Sampling Bulb*, 125 mL capacity with septum port.

7.5 *Personal Sampling Pump*.

7.6 *Gas-Tight Syringe*, 1, 10, 100, 500 mL capacity or other convenient sizes for preparing standards.

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[5] The columns in most portable gas chromatographs are easily interchanged. One manufacturer has an instrument that simultaneously injects onto two user selected column modules.

7.7 *Microlitre Syringes*, 10, 25, 50, 100 µL or other convenient sizes for preparing standards.

7.8 *Gas Sampling Bags*, for preparation of gas standards. Bags constructed of various polymer films, such as polyvinylidene fluoride, fluorinated ethylenepropylene, (tetrafluoroethylene)-fluorocarbon, polyvinylidene chloride, polyethylene and mixed polymer multilayers, with a variety of fittings and capacities (typically 1 to 200 L) are available.

7.9 *Thermal Anemometer, Vane Anemometer, Mass Flowmeter or Pitot Tube*, for measurement of vent velocity.

7.10 *Condensation Trap, Filtering Flask*, 250 or 500 mL polypropylene fitted with a stopper.

7.11 *TFE-Fluorocarbon Tubing*, 6 mm (¼ in.) outside diameter by 5 mm (3⁄16 in.) inside diameter.

7.12 *Data System*, an integral or external computer used for control of operation of a portable gas chromatograph, data reduction, and storage of results.

8. Hazards

8.1 See NFPA 496 for use of electrical equipment in areas classified as hazardous by Article 500 of NFPA 70, National Electrical Code. A purged and pressurized enclosure is required.

9. Calibration

9.1 Suitable knowns may be prepared by the filling of a gas sampling bag with a known volume of air. Inject a known volume of gas or liquid into the bag and knead the bag to mix. Permeation tubes or rigid chambers may also be used for preparation of gas standards. Reference standards in compressed gas cylinders certified as to concentration by the manufacturer are also available. Refer to *Methods of Air Sampling and Analysis*[6] for applicable guidelines for all of these gas standard preparation techniques.

9.2 Although standards of some compounds prepared in gas bags are very stable, others show sample loss during storage due to permeation or surface adsorption. As a general guideline prepare standards fresh daily.

9.3 Prepare at least two reference standards containing varying concentrations of each component. Bracket the expected concentrations of each component in the testing of the process vent, if known.

9.3.1 Connect the gas sampling bag to the inlet or the calibration port of the GC and initiate the analysis. Perform at least triplicate injections of each standard.

9.3.2 The quantitative response of a GC detector may be determined by the measurement of the peak height or peak area using the Data System or electronic integrator.[7]

9.3.3 Following the standard analyze a gas sampling bag containing air only (blank). If carryover is >1 % increase the sampling period (internal GC pump time). Typical sampling periods are 20 to 45 s, however, this parameter must be optimized for each VOC analyzed.

10. Procedure

10.1 *Preparation of the Gas Chromatograph*:

10.1.1 Fill the internal carrier gas reservoir as described by the manufacturer.

10.1.2 Select a carrier gas flow or column pressure and column temperature compatible with the column selected for the separation.

10.1.3 Calibrate the chromatographic column to determine the relative retention times and response of the various compounds of interest.

10.2 *Preparation of the Sampling Train*:

10.2.1 Assemble the sampling train as shown in Fig. 1. Stainless steel or glass may be substituted for the TFE-fluorocarbon transfer line.[8]

10.2.2 For process vents containing high concentrations of higher boiling (>125°C) low vapor pressure (<2 kPa) VOCS a heated transfer line may be necessary. A portable GC with a heated injector is also required.

10.2.3 Recheck the calibration after assembly of the sampling train by connecting an appropriate standard to the inlet of the sample line. If results obtained for the analysis of the standard are not within 15 % relative standard deviation of the expected concentration, check the sampling train for leaks. Flow rate through sampling train is typically 0.5 to 2 L/min.

10.3 *Analysis*:

10.3.1 Set the gas chromatograph at a desired automated sampling interval and sampling period. At the desired time interval, activate the internal vacuum pump of the GC and pull the sample vapors from the sampling bulb. Inject and analyze. It is recommended that the flow rate through the sampling train be set at 2 L/min if the optional condensation trap is installed to minimize sample transfer time and the dilution effect caused by the additional volume of the flask (250 to 500 mL). This ensures that the sample analyzed at the GC is representative of what is currently in the process vent. Permeability of the TFE-fluorocarbon tubing is minimal and can be neglected.[6]

10.3.2 If flow data are not available from the process flowmeter, measure the flow in the vent using a pitot tube, thermal anemometer, or suitable device. If the flow device does not automatically correct readings to standard conditions of 25°C and 101.3 kPa pressure, vent temperature and pressure will also have to be measured. Refer to 2.1 for applicable guidelines.

10.3.3 For continuous monitoring of flow, install the flow probe in center of the vent and send the output signal of the flow measuring device to the data logger for data storage. The center of the vent typically shows the maximum flow rate.

10.3.4 At the end of the sampling period recheck the instrument performance by connecting gas standard to the sample line.[9] If a separate calibration port is available on the portable GC, reanalyze the gas standard every hour during the sampling period. If recovery obtained for standard is <85 % or >115 %, repeat the analysis of the vent after identifying source of the problem. Typical causes of poor recovery include leak in

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[6] Lodge, James P., ed., *Methods of Air Sampling and Analysis*, Intersociety Committee, Lewis Publishers, Inc., 3rd ed., 1988, pp. 15–26.

[7] Most portable GCS are equipped with data systems that automatically generate a calibration curve.

[8] Heated steel lines will degrade or destroy chlorinated organic compounds.

[9] Method 18—Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, 40 CFR 60, App. A, 1994, pp. 792–821.

sample train, partially or completely plugged instrument filter, improper internal pump or injection valve operation, and detector malfunction.

10.3.5 Data reduction, either by peak height or peak area measurement, may now be performed. Some portable GCs automatically develop files that can be directly loaded into an EXCEL or Lotus spreadsheet format. Most data loggers for recording of flow also develop files that can be easily loaded into spreadsheets, which can be combined into one spreadsheet to develop a detailed emission rate profile for each organic compound. An example of a typical spreadsheet is given in Appendix X1.

10.3.6 By direct sampling of process vents with a portable gas chromatograph, process trends and conditions can be monitored and more easily and quickly optimized. A graphical display illustrating how simultaneous monitoring of the inlet and outlet of a water scrubber using two portable gas chromatographs aided optimization of flow rate required to remove an organic compound from a vent stream is shown in Appendix X2. This chart was created in EXCEL from the data shown in Appendix X1.

11. Calculations

11.1 *Calculation of the Concentration of Organic Chemical Vapor Standards in Gas Sampling Bags*:

11.1.1 Calculate the concentration C in parts per million by volume (ppm(v)) as follows:

$$c = \frac{L \times D \times 1000 \times 24.45}{MW \times V} \quad (1)$$

where:

L = volume of liquid added to bag, µL,
D = density of liquid, kg/m^3,
24.45 = molar volume of ideal gas, L/mole, at 25°C and 101.3 kPa pressure (760 mm Hg),
MW = molecular weight of compound, g/mol, and
V = total volume = volume air in bag plus volume of vaporized liquid added, L, and
1000 = 1000 mL/L.

11.2 Calculate the vent flow rate at standard conditions.

11.2.1 For instruments that correct to standard conditions calculate as follows:

$$F = V \times A \times 1000 \quad (2)$$

where:

F = flow, L/min at 25°C and 101.3 kPa pressure (760 mm Hg),
V = air velocity, m/min, and
A = vent cross sectional area, m^2.

11.2.2 For instruments that do not automatically correct to standard conditions:

$$F = \frac{V \times A \times P \times 298 \times 1000}{101.3 \times (T + 273)} \quad (3)$$

where:

P = pressure of vent in kPa, and
T = temperature of vent, °C.

11.3 Calculate the emission rate of organic compound.

11.3.1 Calculate ER, the emission rate in kg/h as follows:

$$ER = \frac{C \times 10^{-6} \times MW \times F \times 60}{24.45 \times 1000} \quad (4)$$

where:

C = concentration of compound, ppm(v) (µL/L),
10^{-6} = conversion factor for L to µL, and
1000 = conversion factor for g to kg.

12. Keywords

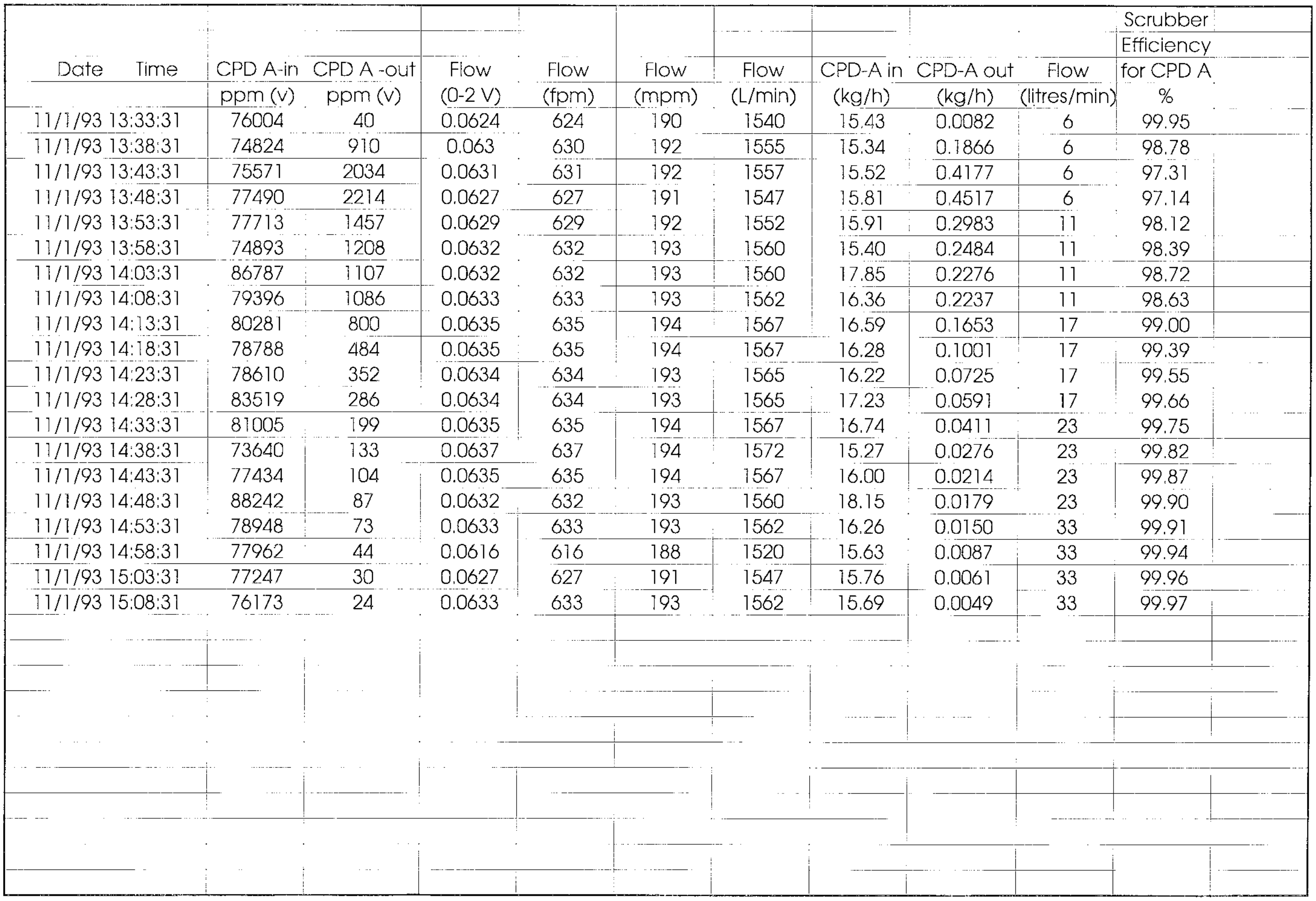
12.1 emissions; emission monitoring; gas chromatography; sampling and analysis

APPENDIXES

(Nonmandatory Information)

X1. EXCEL SPREADSHEET OF PORTABLE GC RESULTS FOR VOC IN PROCESS VENT

X1.1 The data contained in Columns 1 to 3 in Table X1.1 were obtained by loading .dif file created by portable GC into an EXCEL spreadsheet. Column 1 is the date and time the sample was analyzed, while Columns 2 and 3 are the concentrations in ppm(v) of Compound A (CPD-A) found at the inlet and outlet of the scrubber vent. The data in Column 4 were created by loading data stored by data logger for process vent flow into the EXCEL spreadsheet. The data logger stores a voltage reading which has to be converted to a flow reading. Data contained in the other columns are calculated from data in Columns 2 to 4. Column 5 is Vent Flow (ft/min) = 10 000 × Voltage Reading of Data Logger. Flow is at standard conditions of 25°C and 101.3 kPa pressure. Column 6 is vent flow in meters/min (m/min) = .30480 × values in Column 5. Column 7 is flow in standard L/min obtained using Eq Eq 2. Columns 8 and 9 obtained using Eq Eq 4 convert the concentrations in ppm(v) at the inlet and outlet of the scrubber to kg/h entering and exiting the water scrubber. Column 10 is water flow in litres/min. Column 11 is scrubber efficiency = 1 − (Column 9/Column 8) × 100.



Date Time	CPD A-in ppm (v)	CPD A -out ppm (v)	Flow (0-2 V)	Flow (fpm)	Flow (mpm)	Flow (L/min)	CPD-A in (kg/h)	CPD-A out (kg/h)	Flow (litres/min)	Scrubber Efficiency for CPD A %
11/1/93 13:33:31	76004	40	0.0624	624	190	1540	15.43	0.0082	6	99.95
11/1/93 13:38:31	74824	910	0.063	630	192	1555	15.34	0.1866	6	98.78
11/1/93 13:43:31	75571	2034	0.0631	631	192	1557	15.52	0.4177	6	97.31
11/1/93 13:48:31	77490	2214	0.0627	627	191	1547	15.81	0.4517	6	97.14
11/1/93 13:53:31	77713	1457	0.0629	629	192	1552	15.91	0.2983	11	98.12
11/1/93 13:58:31	74893	1208	0.0632	632	193	1560	15.40	0.2484	11	98.39
11/1/93 14:03:31	86787	1107	0.0632	632	193	1560	17.85	0.2276	11	98.72
11/1/93 14:08:31	79396	1086	0.0633	633	193	1562	16.36	0.2237	11	98.63
11/1/93 14:13:31	80281	800	0.0635	635	194	1567	16.59	0.1653	17	99.00
11/1/93 14:18:31	78788	484	0.0635	635	194	1567	16.28	0.1001	17	99.39
11/1/93 14:23:31	78610	352	0.0634	634	193	1565	16.22	0.0725	17	99.55
11/1/93 14:28:31	83519	286	0.0634	634	193	1565	17.23	0.0591	17	99.66
11/1/93 14:33:31	81005	199	0.0635	635	194	1567	16.74	0.0411	23	99.75
11/1/93 14:38:31	73640	133	0.0637	637	194	1572	15.27	0.0276	23	99.82
11/1/93 14:43:31	77434	104	0.0635	635	194	1567	16.00	0.0214	23	99.87
11/1/93 14:48:31	88242	87	0.0632	632	193	1560	18.15	0.0179	23	99.90
11/1/93 14:53:31	78948	73	0.0633	633	193	1562	16.26	0.0150	33	99.91
11/1/93 14:58:31	77962	44	0.0616	616	188	1520	15.63	0.0087	33	99.94
11/1/93 15:03:31	77247	30	0.0627	627	191	1547	15.76	0.0061	33	99.96
11/1/93 15:08:31	76173	24	0.0633	633	193	1562	15.69	0.0049	33	99.97

FIG. X1.1 EXCEL Spreadsheet of Portable GC Results for VOC in Process Vents

X2. GRAPH OF KG/H OF VOC INTO AND OUT OF WATER SCRUBBER VERSUS FLOW RATE OF WATER THROUGH SCRUBBER

X2.1 The graph (Fig. X2.1) is a plot of Columns 8 and 9 (kg/h of Compound A entering and exiting the water scrubber) of Table X1.1 versus the flow rate of water through the scrubber (Column 10). It illustrates how direct monitoring of a process vent with a portable GC can aid optimization of process variables such as scrubber flow rate.

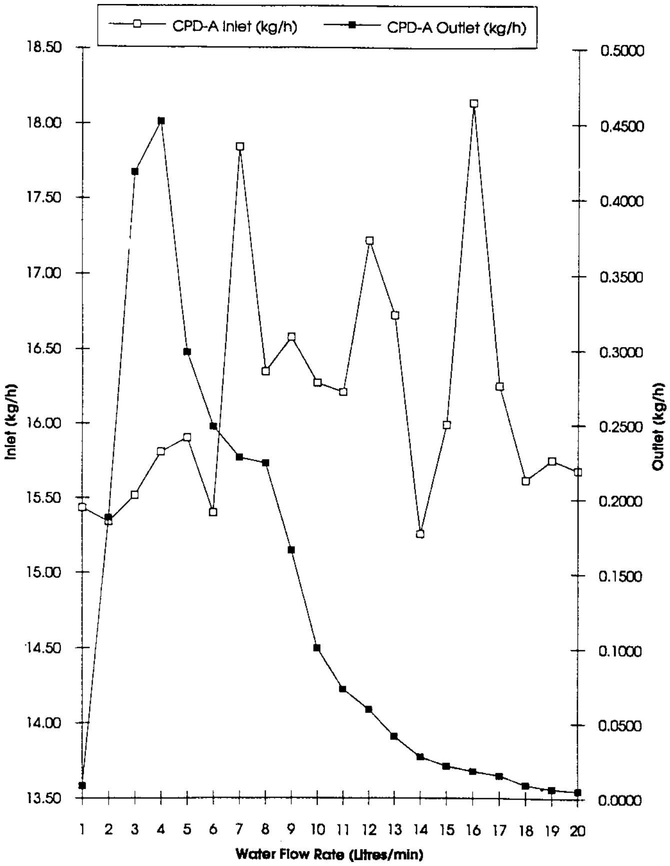


FIG. X2.1 Optimization of Water Scrubber Flow Rate

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