

## VIII. REFERENCES

1. Marsden J, Cuthbertson AC: The vapor pressure of vinyl acetate. *Can J Res* 9:419-23, 1933
2. Rhum D: Poly(vinylacetate), in Kirk-Othmer Encyclopedia of Chemical Technology, ed 2 rev. New York, Interscience Publishers, 1970, vol 21, pp 317-53
3. Gofmekler VA: [Maximum admissible concentration of acetates in the atmosphere.] *Gig Sanit* 25:9-15, 1960 (Rus)
4. Summary of Responses of Animals and Humans to the Vapors of Vinyl Acetate. Unpublished report submitted to American Conference of Governmental Industrial Hygienists by Carnegie-Mellon University, Mellon Institute, Pittsburgh, Pa, Oct 1968, 3 pp
5. Properties and Essential Information for Safe Handling and Use of Vinyl Acetate, Chemical Safety Sheet Data SD-75, rev. Washington, DC, Manufacturing Chemists' Association, General Safety Committee, 1970, 15 pp
6. Fassett DW: Esters, in Patty FA (ed.): Industrial Hygiene and Toxicology, ed 2, rev; Toxicology (Fassett DW, Irish DD, eds.). New York, Interscience Publishers, 1963, vol 2, pp 1874-81
7. Hawley GG (ed.): The Condensed Chemical Dictionary, ed 9, rev. New York, Van Nostrand Reinhold Co, 1977, p 916
8. Leonard EC: Vinyl acetate, in Leonard EC (ed.): Vinyl and Diene Monomers. New York, Wiley-Interscience, 1970, Part 1, pp 263-363
9. Weast RC (ed.): CRC Handbook of Chemistry and Physics--A Ready-Reference Book of Chemical and Physical Data, ed 55. Cleveland, CRC Press Inc, 1974, p C-80,E-74 to E-80
10. Frey HE, Wolfe AJ: Vinyl acetate, polyvinyl acetate, and polyvinyl alcohol, in Chemical Economics Handbook. Menlo Park, Calif, SRI International, 1977, pp 580.1871C to 580.1871F, 580.1872A to 580.1872Z, 580.1873A to 580.1873M
11. Preliminary Report on US Production of Selected Synthetic Organic Chemicals--November, December, and Cumulative Totals, 1977. US International Trade Commission, 1978, pp 1,3
12. Vinyl Acetate. Unpublished report submitted to NIOSH by Celanese Corp, Celanese Chemical Co, Product Standards, New York, Sep 1976, 36 pp

13. Miller SA: Chemicals from acetylene. Chem Ind (London) 41:4-16, 1963
14. Carpenter CP, Smyth HF Jr, Pozzani UC: The assay of acute vapor toxicity, and the grading and interpretation of results on 96 chemical compounds. J Ind Hyg Toxicol 31:343-46, 1949
15. Ekel GJ, Teichner WH: An Analysis and Critique of Behavioral Toxicology in the USSR, DHEW (NIOSH) Publication No. 77-160. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Division of Biomedical and Behavioral Science, 1976, 130 pp
16. Reinhardt CF: Vinyl Acetate Survey--Niagara Falls Plant, Haskell Laboratory Report No. 138-69, in Information Concerning the Development of the Criteria Document and Recommended Health Standard for Vinyl Acetate, EI du Pont de Nemours and Co Inc, Employee Relations Dept, Safety and Fire Protection Division, Engineering Section, Wilmington, Del, Mar 1976, 2 pp
17. Toxicology Studies--Vinyl Acetate HQ. New York, Union Carbide Corp, Industrial Medicine and Toxicology Dept, 1958, 2 pp
18. Deese DE, Joyner RE: Vinyl acetate--A study of chronic human exposure. Am Ind Hyg Assoc J 30:449-57, 1969
19. Report of Toxicity of Vinyl Acetate. Unpublished report submitted to American Conference of Governmental Industrial Hygienists by EI du Pont de Nemours and Co Inc, Central Research and Development Dept, Haskell Laboratory for Toxicology and Industrial Medicine, Jan 1967, 7 pp
20. Gage JC: The subacute inhalation toxicity of 109 industrial chemicals. Br J Ind Med 27:1-18, 1970
21. Goldstein I, David V, Rotaru G: [Experimental research on the combined action of vinyl acetate and acetic acid,] in Activiatea Stintifica a Institutului de Igiena, Bucharesti 1927-1967. Bucharest, Rumania, Editau Medicala, 1968, pp 309-11 (Rum) (Abst)
22. Bartenev VD: [The effect of vinyl acetate on the central nervous system of rabbits.] Gig Tr Prof Zabol 8:63-66, 1957 (Rus)
23. Goeva OE: Maximum permissible concentration of vinyl acetate in water basins. Hyg Sanit (USSR) 31:209-14, 1966
24. Maltoni C, Lefemine G: Carcinogenicity bioassays of vinyl chloride--I. Research plan and early results. Environ Res 7:387-405, 1974
25. Maltoni C: Carcinogenicity of vinyl chloride--Current results--Experimental evidence. Adv Tumor Prev Detect Charact 3:216-37, 1976

26. Bartsch H, Malaveille C, Montesano R: The predictive value of tissue-mediated mutagenicity assays to assess the carcinogenic risk of chemicals, in Montesano R, Bartsch H, Tomatis L (eds.): Screening Tests in Chemical Carcinogenesis, IARC Scientific Publication No. 12. Lyon, France, World Health Organization, International Agency for Research on Cancer, 1976, pp 467-91
27. Filov VA: [On the fate of complex esters of vinyl alcohol and fatty acids in the organism.] Gig Tr Prof Zabol 3:42-46, 1959 (Rus)
28. Rostovskii EN, Ushakov SN, Barinova AN: [The properties of a series of complex vinyl esters--Communication 1. Polymerization and saponification rate of monomers.] Izv Akad Nauk SSSR Ser Khim, 59:59-63, 1958 (Rus)
29. Murphy SD, DuBois KP: Quantitative measurement of inhibition of the enzymatic detoxification of malathion by EPN (ethyl p-nitrophenyl thionobenzenephosphonate). Proc Soc Exp Biol Med 96:813-18, 1957
30. Murphy SD, Anderson RL, DuBois KP: Potentiation of toxicity of malathion by triorthotolyl phosphate. Proc Soc Exp Biol Med 100:483-87, 1959
31. Murphy SD: Malathion inhibition of esterases as a determinant of malathion toxicity. J Pharmacol Exp Ther 156:352-365, 1967
32. Oi S, Satomura Y: Substrate specificity, mode of action, and of inhibition by organic acids of purified acetylcysteine aminohydrolase from Sclerotinia fungus. Agric Biol Chem 31:561-68, 1967
33. Boyland E, Chasseaud LF: The effect of some carbonyl compounds on rat liver glutathione levels. Biochem Pharmacol 19:1526-28, 1970
34. Boyland E, Chasseaud LF: Enzyme-catalysed conjugations of glutathione with unsaturated compounds. Biochem J 104:95-102, 1967
35. Chasseaud LF: The nature and distribution of enzymes catalyzing the conjugation of glutathione with foreign compounds. Drug Metab Rev 2:185-220, 1973
36. Tiunova LV, Rummyantsev AP: Changes in rhythm of liver enzyme activity in albino rats during chronic exposure to vinyl acetate. Bull Exp Biol Med (USSR) 79:453-55, 1975
37. Criteria for a Recommended Standard....Occupational Exposure to Vinyl Halides. To be published by US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health

38. Thomas LB, Popper H, Berk PD, Selikoff I, Falk H: Vinyl-chloride-induced liver disease--From idiopathic portal hypertension (Banti's syndrome) to angiosarcomas. *N Engl J Med* 292:17-22, 1975
39. Makk L, Creech JL, Whelan JG Jr, Johnson MN: Liver damage and angiosarcoma in vinyl chloride workers--A systematic detection program. *J Am Med Assoc* 230:64-68, 1974
40. Falk H, Creech JL Jr, Heath CW Jr, Johnson MN, Key MM: Hepatic disease among workers at a vinyl chloride polymerization plant. *J Am Med Assoc* 230:59-63, 1974
41. Lee CC, Bhandari JC, Winston JM, House WB, Peters PJ, Dixon RL, Woods JS: Inhalation Toxicity and Carcinogenicity of Vinyl Chloride and Vinylidene Chloride. Unpublished report submitted to NIOSH by Lee CC, Midwest Research Institute, Pharmacology and Toxicology, Kansas City, Mo, May 1977, 46 pp
42. Dorato MA: Twelve Month Interim Report--Oncogenic Potential of Vinyl Bromide During Inhalation Exposure, rev. Report submitted to Vinyl Bromide Task Force by Huntingdon Research Center, New York, Dec 1977, 258 pp
43. Bartsch H, Malaveille C, Montesano R: Human, rat and mouse liver-mediated mutagenicity of vinyl chloride in *S. typhimurium* strains. *Int J Cancer* 15:429-37, 1975
44. Greim H, Bonse G, Radwan Z, Reichert D, Henschler D: Mutagenicity in vitro and potential carcinogenicity of chlorinated ethylenes as a function of metabolic oxirane formation. *Biochem Pharmacol* 24:2013-17, 1975
45. Bartsch H, Montesano R: Mutagenic and carcinogenic effects of vinyl chloride. *Mutat Res* 32:93-113, 1975
46. Simmon VF, Mangham R: Mutagenic Activity of Vinyl Bromide. Unpublished report submitted to NIOSH by Simmon VF, SRI International, Microbial Genetics, Menlo Park, Calif, Aug 1977, 10 pp
47. Sigman CC, Helmes CT, Mill T, Gould CW: Structure-Activity Relationships. Unpublished report submitted to NIOSH by Sigman CC, SRI International, Menlo Park, Calif, Dec 1977, 28 pp
48. Dahl GA, Miller EC, Miller JA: Vinyl carbamate, a potent carcinogen and a possible urethan metabolite in the mouse. *Proc Am Assoc Cancer Res Am Soc Clin Oncol* 18:6, 1977 (Abst)
49. Gordon SJ, Meeks SA: A study of gaseous pollutants in the Houston, Texas area, in Proceedings of the 79th National Meeting of the American Institute of Chemical Engineers, Houston, Mar 16-20, 1975, 11 pp

50. Pervier JW, Barley RC, Field DE, Friedman BM, Morris RB, Schwartz WA: Survey Reports on Atmospheric Emissions from the Petrochemical Industry--Volume IV, Report No. EPA-450/3-73-005-d. Springfield, Va, US Dept of Commerce, National Technical Information Service, 1974, 278 pp (NTIS PB 245 630)
51. Plant observation reports and evaluation. Menlo Park, Calif, SRI International, Feb 1978, 108 pp (submitted to NIOSH under contract No. CDC-99-74-31)
52. Vinyl acetate--Physical and Chemical Analysis Method No. 278, in NIOSH Manual of Analytical Methods. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Measurements Research Branch, 1978, 8 pp (unpublished)
53. Horacek J: [Polarographic determination of vinyl acetate.] Plaste Kautsch 9:116-17, 1962 (Ger)
54. Bokov AN, Fedorchuk SY, Prokopenko VA: Sanitary-chemical assessment of polyvinyl acetate seamless floors with addition of carbamide resins. Hyg Sanit (USSR) 30:202-08, 1965
55. Horacek J: [Chromatographic separation of some monomers.] Cesk Hyg 13:609-12, 1968 (Cze)
56. Osokina SK, Erisman FF: [Chromatographic determination of vinyl acetate in air with preliminary mercurization in a medium of low aliphatic alcohols.] Gig Sanit 37:72-74, 1972 (Rus)
57. Petrova LI, Boikova ZK: [Determination of small amounts of vinyl acetate in air, water, alcohol solutions, and foods.] Gig Sanit 6:48-49, 1975 (Rus)
58. Andronov BY, Yudina AK: [Determination of vinyl acetate, formaldehyde and methanol in the air in the presence of butyraldehyde or acetaldehyde and hydrogen chloride.] Nauchn Rab Inst Okhr Tr Vses Tsentr Sov Prof Soyuzov 5:77-81, 1964 (Rus)
59. Gronsberg ES: [Atmospheric determination of some organic compounds which form formaldehyde.] Nov Obl Prom Sanit Khim, pp 8-14, 1969 (Rus)
60. Smith B, Dahlen J: Gas chromatographic analysis of a mixture of acetaldehyde, acetone, vinyl acetate, acetic acid, paraldehyde, acetic anhydride, and ethylidene diacetate. Acta Chem Scand 17:801-04, 1963
61. West PW, Sen B, Sant BR, Mallik KL, Sen Gupta JG: A catalog of retention times of a number of organic compounds. J Chromatogr 6:220-35, 1961

62. Bollini M, Seves A, Focher B: [Determination of free monomers in aqueous emulsions of synthetic polymers or copolymers.] Ind Carta 12:234-40, 1974 (Ita)
63. Germaine RW, Haken JK: Gas chromatography of homologous esters--Part II. Unsaturated esters. J Chromatogr 43:43-47, 1969
64. May RW, Pearson EF, Porter J, Scothern MD: A reproducible pyrolysis gas-chromatographic system for the analysis of paints and plastics. Analyst 98:364-71, 1973
65. McCammon CS Jr: Evaluation of Portable, Direct-Reading Combustible Gas Meters, HEW Publication No. (NIOSH) 74-107. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Division of Laboratories and Criteria Development, 1974, 48 pp
66. Leichnetz K (ed.): Detector Tube Handbook--Air Investigations and Technical Gas Analysis with Draeger Tubes, ed 3. Luebeck, Federal Republic of Germany, Draegerwerk Ag, 1976, 190 pp
67. Bendix Gastec Precision Gas Detector System Manual. Warwick, RI, National Environmental Instruments Inc, Health and Safety Instrumentation, p 73 (undated)
68. Willey MA, McCammon CS Jr: Evaluation of Portable, Direct-Reading Hydrocarbon Meters (Flame Ionization, Photoionization, and Infrared Detectors), HEW Publication No. (NIOSH) 76-166. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, 1976, 84 pp
69. Analytical Data for Gases and Vapors with No Established OSHA Exposure Limits. S. Norwalk, Conn, Wilks Scientific Corp, 1977, 1 p
70. Organic Vapor Analyzers, Brochure No. CS-079-7616. Arkansas City, Kans, Century Systems Corp, 5 pp (undated)
71. Trace Gas Analysis by Photoionization. Newton Upper Falls, Mass, HNU Systems Inc, 1975, 6 pp
72. American Conference of Governmental Industrial Hygienists, Committee on Industrial Ventilation: Industrial Ventilation--A Manual of Recommended Practice, ed 14. Lansing, Mich, ACGIH, 1976, pp 1-1 to 14-8
73. American National Standards Institute Inc: Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971. New York, ANSI, 1971, 63 pp

74. Hagopian JH, Bastress EK: Recommended Industrial Ventilation Guidelines, DHEW Publication No. (NIOSH) 76-162. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, 1976, 330 pp
75. National Electrical Code--1978 Edition, NFPA No. 70. Boston, National Fire Protection Association, 1977, 623 pp
76. Chemical Data Guide for Bulk Shipment by Water, No. CG-388. US Dept of Transportation, United States Coast Guard, 1976, pp 273,299-302
77. Vinyl acetate explosion and fire--Fatality, case history No. 384, in Safety and Fire Protection Committee: Case Histories of Accidents in the Chemical Industry. Washington, DC, Manufacturing Chemists' Association, 1962, vol 1, pp 106-07
78. Chicago vinyl acetate incident, in Vervalin CH (ed.): Fire Protection Manual for Hydrocarbon Processing Plants. Houston, Gulf Publishing Co, 1964, p 358
79. Joint AIHA-ACGIH Respiratory Protective Devices Committee: Respiratory Protective Devices Manual. Ann Arbor, Mich, American Industrial Hygiene Association and American Conference of Governmental Industrial Hygienists, 1963, 162 pp
80. Nelson GO, Harder CA: Respirator cartridge efficiency studies--VI. Effect of concentration. Am Ind Hyg Assoc J 37:205-16, 1976
81. American Conference of Governmental Industrial Hygienists: Threshold Limit Values of Airborne Contaminants and Intended Changes Adopted by ACGIH for 1969. Cincinnati, ACGIH, 1969, p 18
82. American Conference of Governmental Industrial Hygienists: Threshold Limit Values of Airborne Contaminants and Physical Agents with Intended Changes Adopted by ACGIH for 1971. Cincinnati, ACGIH, 1971, p 27
83. American Conference of Governmental Industrial Hygienists: TLV's--- Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1976. Cincinnati, ACGIH, 1976, p 30
84. American Conference of Governmental Industrial Hygienists, Committee on Threshold Limit Values: Documentation of Threshold Limit Values for Substances in Workroom Air, ed 3, 1971. Cincinnati, ACGIH, 2nd printing, 1974, pp 276-77
85. Occupational Exposure Limits for Airborne Toxic Substances--A Tabular Compilation of Values from Selected Countries--Occupational Safety and Health Series No. 37. Geneva, International Labour Office, 1977, pp 33,214-15

## IX. APPENDIX I

### METHOD FOR SAMPLING AND ANALYSIS OF VINYL ACETATE IN AIR

This analytical method for vinyl acetate is adapted from NIOSH Method No. P&CAM 278 (classification E) [52]. A Class E method is defined by NIOSH as "Proposed: A new, unproved, or suggested method not previously used by industrial hygiene analysts but which gives promise of being suitable for the determination of a given substance." The proposed validation range is 8-210 mg/cu m in a 1.5-liter sample. Although the method has not yet been validated at 7 mg/cu m, which is one-half of the recommended ceiling limit, it shows promise of being usable for determining vinyl acetate at this concentration.

#### Principle of the Method

A known volume of air is drawn through a tube containing a Chromosorb 107 to trap the vinyl acetate present. The vinyl acetate is thermally desorbed into a 300-ml chamber. An aliquot of the desorbed vapor is injected into a gas chromatograph. The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

#### Range and Sensitivity

(a) Sample loadings of between 2 and 332  $\mu\text{g}$  of vinyl acetate for each sampling device are acceptable. Samples have been successfully collected from dynamically generated atmospheres of vinyl acetate over the concentration range of 8.2-206 mg/cu m when the relative humidity of the sampled air was greater than 80%.

(b) The slope of a typical calibration curve (integrator response vs mass of vinyl acetate in the sample tube) was 687 volt-seconds/g. The sensitivity of the flame ionization detector was  $4.04 \times 10^{-6}$  coulombs/g of vinyl acetate (\* indicates an exponent).

(c) The lowest quantifiable level was determined to be 0.5  $\mu\text{g}$  of vinyl acetate/300-mg bed of Chromosorb 107. At this loading the relative standard deviation of replicate samples was better than 10%.

#### Interferences

(a) When two or more substances are known or suspected to be present in the air sampled, such information should be transmitted with the sample, because the substances may interfere with the analysis of vinyl acetate.



(b) Any substance that has the same retention time as vinyl acetate at the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

(c) If the possibility of interference exists, separation conditions, eg, column packing, temperature, carrier flow, or detector, must be changed to circumvent the problem.

#### Precision and Accuracy

(a) The pooled relative standard deviation of the sampling and analytical method was 8.1%. This reflects the precision of sampling and analysis of 50 samples of vinyl acetate collected with calibrated personal sampling pumps from humid atmospheres (>80%) over the concentration range of 8-206 mg/cu m. The relative standard deviation of samples collected from atmospheres averaging 8.6 mg/cu m (range 8.2-9.0) was 9.5%, from atmospheres averaging 24.3 mg/cu m (range 18.6-39.2) was 8.0%, and from atmospheres averaging 181 mg/cu m (range 159-206) was 5.9%.

(b) The concentration of the sampled air was independently determined using a gas-phase infrared analyzer. The samples were collected from humid air and stored at room temperature. The determination averaged 7% high, 5% high, and 4% low when analyzed on days 1, 7, and 14, respectively. Thus, the sample displayed a 0.8%/day storage loss when stored at room temperature. This loss can be attributed to the analyte degrading in the presence of water, because samples spiked with 18  $\mu\text{g}$  of vinyl acetate in "dry" hexane gave 98% recovery when stored for 14 days at room temperature.

(c) The breakthrough volume and therefore the capacity of Chromosorb 107 for vinyl acetate decreased with increasing relative humidity. Under the most adverse conditions tested, 83% relative humidity, the breakthrough volume was found to be 4.0 liters when an atmosphere of vinyl acetate at 113 mg/cu m was sampled at 0.125 liter/minute.

#### Advantages and Disadvantages of the Method

(a) The sampling device is small, portable, and involves no liquids.

(b) The samples are analyzed using a quick instrumental method and the sampling tubes can be reused after the analysis is completed.

(c) Many of the interferences can be eliminated by altering chromatographic conditions.

(d) The precision of the method is limited by the reproducibility of the pressure drop across the sampling tubes. Variations in pressure drop will

affect the flowrate. The reported sample volume will be imprecise because the pump is usually calibrated for one tube only.

(e) The amount of sample that can be collected is limited by the capacity of the sampling device. When the amount of vinyl acetate found on the backup section exceeds 10% of the amount found on the front section, the possibility of sample loss exists. Migration from the front to the backup section is not a problem because the sections are separated and individually capped immediately after sampling.

### Apparatus

(a) Personal sampling pump capable of accurate performance at 0.1 liter/minute. The pump must be calibrated with a representative sampling device in line, and the pump battery must be fully charged prior to being used.

(b) Chromosorb 107 sampling tubes. Individual front and backup tubes (Century Systems Corporation "Flare" tubes or equivalent) are used. The front section is a stainless steel tube 7.3 cm long with a 6-mm outer diameter, a 4-mm inner diameter, and a 45-degree flare at one end. The backup section is a chrome-plated nickel tube 3 cm long with a 6-mm outer diameter, a 4-mm inner diameter, a 45-degree flare at one end and a hose connection at the other end. Each tube has a permanent metal frit in the outlet end of the tube. The front section contains 300 mg of prewashed Chromosorb 107 held in place with a removable metal frit. The backup section contains 50 mg of prewashed Chromosorb 107 held in place with a plug of silylated glass wool. The sampling device is assembled by joining the front and backup sections with a nylon nut and fitting. A hollow nylon ferrule is placed between the two sections. The pressure drop across the tubes must be less than 10 inches of water at a flowrate of 0.1 liter/minute. The Chromosorb 107 is washed in a Soxhlet extractor for 8 hours with water, 8 hours with methanol, and 8 hours with dichloromethane. The sorbent is then dried overnight in a vacuum oven. The tubes are loaded with sorbent and thermally purged for 2 minutes with helium at 150 C. After cooling in a closed container, the ends are capped.

(c) Thermal desorber equipped with thermostatted desorbing oven, 300-ml sample reservoir, and a 2-ml gas sampling loop (Century Systems Corporation Programmed Thermal Desorber or equivalent).

(d) Gas chromatograph equipped with a flame-ionization detector and electronic integrator.

(e) Gas-chromatographic column (20-feet x 1/8-inch outer diameter) made of silanized stainless steel and packed with 10% FFAP on 80/100 mesh Chromosorb W AW.

(f) Vials, 1.5-ml, with aluminum serum cups equipped with Teflon-lined silicone rubber septa.

(g) Microliter syringes, 10- $\mu$ l and convenient sizes for making standards.

(h) Pipette, 1,000- $\mu$ l, with disposable plastic tips.

(i) U-tube, glass with at least one hose connection, approximately 75-ml internal volume.

(j) Pump capable of drawing 200 ml/minute through the front section of the sampling device.

(k) Gas bag, 10-liter volume for helium purge gas.

(l) Test tubes with close-fitting plastic caps.

(m) Ring stand with clamps.

### Reagents

Whenever possible, reagents used should be ACS Reagent Grade or better.

(a) Vinyl acetate, practical, inhibited with hydroquinone and freshly distilled before use.

(b) Hexane (ultraviolet grade).

(c) Helium, Bureau of Mines Grade A.

(d) Hydrogen, prepurified.

(e) Air, filtered and compressed.

### Procedure

(a) Cleaning of equipment. All nondisposable glassware used for the laboratory analysis of vinyl acetate is washed with detergent and rinsed thoroughly with tapwater and distilled water.

(b) Collection and shipping of samples.

(1) Immediately before sampling, remove the plastic caps from the inlet and outlet ends of the sampling tube.

(2) Connect the tube to the sampling pump using a short piece of flexible tubing. The backup section is positioned nearest the pump. The sampling tube is kept vertical during sampling to prevent channeling through the device.

(3) Air being sampled must not pass through any hose or tubing before entering the sampling device.

(4) The temperature, pressure, and volume of air sampled is measured and reported. The volume sampled should not exceed 3 liters, sampled at a flowrate of 0.1 liter/minute or less. Record either the flowrate and sampling time or the initial and final stroke readings and the volumetric stroke factor.

(5) Immediately after sampling, disassemble the two sections, cap the sections with plastic caps, and label the sections. Do not use rubber caps.

(6) For every 10 samples taken, handle one sampling device in the same manner as the samples (uncap, disassemble, cap, label, and transport); however, do not sample any air through this device. Label this device as a blank.

(7) Samples received at the laboratory are logged in and analyzed as soon as possible. Samples stored at room temperature for 14 days exhibit an 11% loss of analyte.

(c) Analysis of Samples

(1) Preparation of samples. Remove the caps from either a front or a back section. Wipe the outside of the tube with a clean laboratory wiper.

(2) Thermal desorber conditions. Typical operating conditions for the thermal desorber are:

- (A) 150 C desorbing oven temperature
- (B) 70 ml/minute desorbing rate, helium gas
- (C) 160 C transfer line temperature
- (D) 15 second pressure equalization time

(3) Gas-chromatographic conditions. Typical operating conditions for the gas chromatograph are:

- (A) 33 ml/minute helium carrier gas flowrate
- (B) 40 ml/minute hydrogen flow to detector
- (C) 435 ml/minute airflow to detector
- (D) 160 C injector temperature
- (E) 160 C manifold (detector) temperature
- (F) 60 C oven temperature

Under these conditions, the capacity ratio for vinyl acetate should be 4.4.

(4) Thermal desorption of samples. Wipe off the tube and insert it in the desorbing oven. Desorb with helium at atmospheric pressure. The helium is stored in the 10-liter gas bag. Desorbing with air chars the Chromosorb and renders it unsuitable for reuse.

(5) Injection. Inject a 2-ml aliquot of the desorbed vapors into the gas-chromatographic column. Since the desorbed vapors are stored in a reservoir, as many as five replicate injections of each sample can be made.

(6) Measurement of area. Measure the area of the sample peak with an electronic integrator or other suitable technique of area measurement. The results are read from a standard curve as prepared in subsection (d)(4).

(7) Preparation for next sample. After satisfactory analysis is obtained, purge the thermal desorber with helium for 2 minutes. Remove the tube from the desorbing oven, place it in a test tube and cap the test tube. When the tube is cool, remove it from the test tube and cap it with the plastic caps.

#### (d) Calibration and Standardization

(1) It is convenient to express the concentration in terms of  $\mu\text{g}$  of vinyl acetate/sample tube. Standard curves are prepared by loading clean sampling tubes (front sections) with known amounts of vinyl acetate. The density of vinyl acetate ( $0.932 \text{ mg}/\mu\text{l}$  at  $20 \text{ C}$ ) is used to convert the volume taken to mass.

(2) Preparation of standards. Pipet 1.00-ml aliquots of hexane into clean glass vials. Crimp the vials shut with an aluminum serum cap equipped with a Teflon-lined silicone rubber septum. Inject either 25, 10, 5, or  $1 \mu\text{l}$  of freshly distilled vinyl acetate into each vial. These standard solutions are freshly prepared for each analysis.

(3) Loading the standard. Support a U-tube on a ring stand. Using a short length of tubing, attach the outlet end of a clean front section of a sampling tube to a small pump. The inlet end of the clean front section is attached to the side of the U-tube that has the hose connection. Use the solvent-flush technique to withdraw a  $2\text{-}\mu\text{l}$  aliquot of a standard solution. Turn on the pump and inject this  $2\text{-}\mu\text{l}$  aliquot into the end of the U-tube farthest from the sampling tube. Sweep enough air through the U-tube (2 minutes at  $200 \text{ ml/minute}$ , approximately five volume changes) to ensure that all the vinyl acetate is loaded on the sample tube. Stop the pump, remove the sample tube, cap both ends, and label. This tube now contains a known amount of vinyl acetate.

(4) Standardization. Analyze each tube from subsection (d)(3) as in subsection (c)(3). The standard curve is obtained by plotting the amount of vinyl acetate loaded on a tube vs the peak area found. If conditions warrant, prepare standards at higher or lower concentrations.

(e) Calculations

(1) The sample weight in  $\mu\text{g}$  is read from the standard curve.

(2) Blank corrections are not expected. If the analysis shows a blank correction is needed, the correction is:

$$WF = W_s - W_b$$

where:

WF = corrected amount ( $\mu\text{g}$ ) on the front section of the sample tube.

W<sub>s</sub> = amount ( $\mu\text{g}$ ) found on the front section of the sample tube.

W<sub>b</sub> = amount ( $\mu\text{g}$ ) found on the front section of the blank sample tube.

A similar procedure is followed for the backup sections.

(3) The concentration, C, of vinyl acetate in the air sampled is expressed in mg/cu m, which is numerically equal to  $\mu\text{g/liter}$ .

$$C = \frac{WF + WB}{V}$$

where:

WF = corrected amount of vinyl acetate found on front section in  $\mu\text{g}$ .

WB = corrected amount of vinyl acetate found on backup section in  $\mu\text{g}$ .

V = volume of air sampled in liters.

(4) If desired the results may be expressed in ppm at 25 C (298 K) and 760 mmHg.

$$C(\text{ppm}) = C (\mu\text{g/l}) \times \frac{24.45}{86.1} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure of air sampled in mmHg.

T = temperature of air sampled in degrees C.

24.45 = molar volume at 25 C and 760 mmHg in liters/mole.

86.1 = molecular weight of vinyl acetate in g/mole.

## X. APPENDIX II

### MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

#### (a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

#### (b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole

mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 F (21.1 C); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if



possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill" or "incineration." Warnings such as "comply with local, state, and Federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified

as to type and NIOSH or Mine Safety and Health Administration approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous substance. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

--


## MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO EMERGENCY TELEPHONE NO	
ADDRESS		
<b>TRADE NAME</b>		
<b>SYNONYMS</b>		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT (760 MM HG)		MELTING POINT
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H <sub>2</sub> O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

<b>IV FIRE AND EXPLOSION DATA</b>				
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
<b>V HEALTH HAZARD INFORMATION</b>				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN				
INHALATION				
INGESTION				
NOTES TO PHYSICIAN				

<b>VI REACTIVITY DATA</b>	
CONDITIONS CONTRIBUTING TO INSTABILITY	
INCOMPATIBILITY	
HAZARDOUS DECOMPOSITION PRODUCTS	
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION	
<b>VII SPILL OR LEAK PROCEDURES</b>	
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	
NEUTRALIZING CHEMICALS	
WASTE DISPOSAL METHOD	
<b>VIII SPECIAL PROTECTION INFORMATION</b>	
VENTILATION REQUIREMENTS	
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT	
RESPIRATORY (SPECIFY IN DETAIL)	
EYE	
GLOVES	
OTHER CLOTHING AND EQUIPMENT	

**IX SPECIAL PRECAUTIONS**

PRECAUTIONARY  
STATEMENTS

OTHER HANDLING AND  
STORAGE REQUIREMENTS

PREPARED BY \_\_\_\_\_

ADDRESS \_\_\_\_\_

DATE \_\_\_\_\_

## XI. TABLES AND FIGURES

TABLE XI-1  
PHYSICAL AND CHEMICAL PROPERTIES OF VINYL ACETATE

---

Molecular formula	CH <sub>3</sub> COOCH=CH <sub>2</sub>
Molecular weight	86.1
Appearance	Clear, colorless liquid
Odor	Pleasant, sweet to sharp, irritating
Boiling point	72.7 C
Melting (freezing) point	-100.2 C
Vapor density (air = 1)	2.97
Specific gravity	0.9338 at 20 C*
Vapor pressure	100 mmHg at 21.5 C (see Figure XI-1)
Refractive index	1.3952 at 20 C
Viscosity	0.43 centipoise at 20 C
Heat of vaporization	90.6 cal/g at 72.7 C
Heat of combustion	5.75 kcal/g
Heat of polymerization	21.3 kcal/mole
Solubility	2.5 g/100 ml water at 20 C; soluble in most organic solvents
Explosive limits (in air, by volume)	2.6-13.4%
Flashpoint (open cup)	-5.5 C
Autoignition temperature	427 C
Conversion factors	1 mg/cu m = 0.284 ppm 1 ppm = 3.5 mg/cu m

---

\*Density at 20 C given as 0.982 in reference 52

Adapted from references 1,2,5-9,12

TABLE XI-2

OCCUPATIONS WITH POTENTIAL EXPOSURE  
TO VINYL ACETATE

---

Chemical-synthesis workers  
Equipment cleaners  
Equipment repairers  
Maintenance workers  
Monomer-containing-aerosol producers  
Monomer-containing-aerosol users  
Monomer loaders and unloaders  
Monomer production workers  
Monomer samplers and gagers  
Monomer transport workers  
Polymer compounders  
Polymer fabricators  
Polymer loaders and unloaders  
Polymer packagers  
Polymer processors  
Polymer production workers  
Polymer transport workers  
Quality-control-laboratory workers  
Warehouse workers

---

Adapted from references 2,5,8



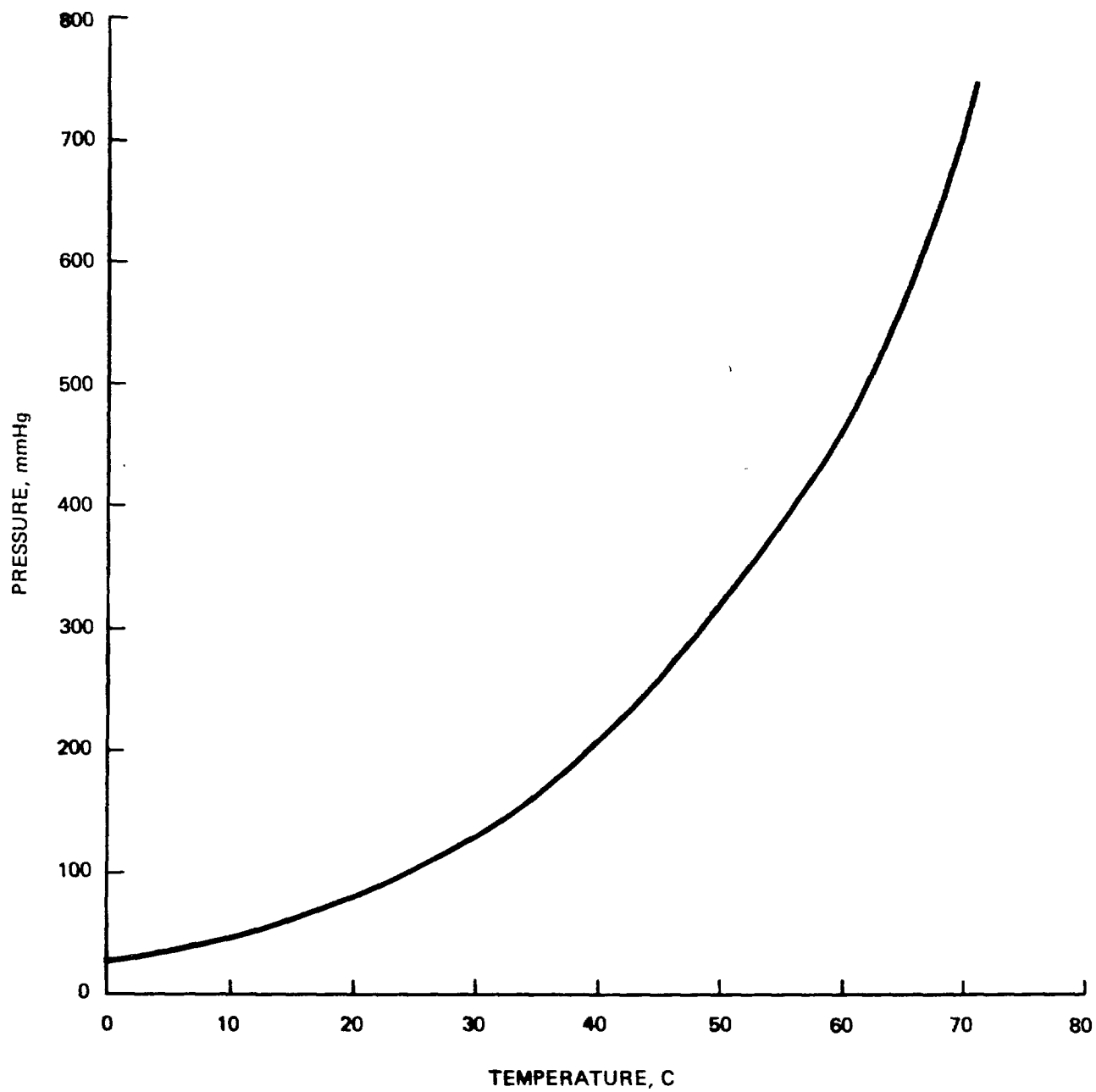


FIGURE XI-1

VAPOR PRESSURE OF VINYL ACETATE VS TEMPERATURE

Adapted from references 1 and 5

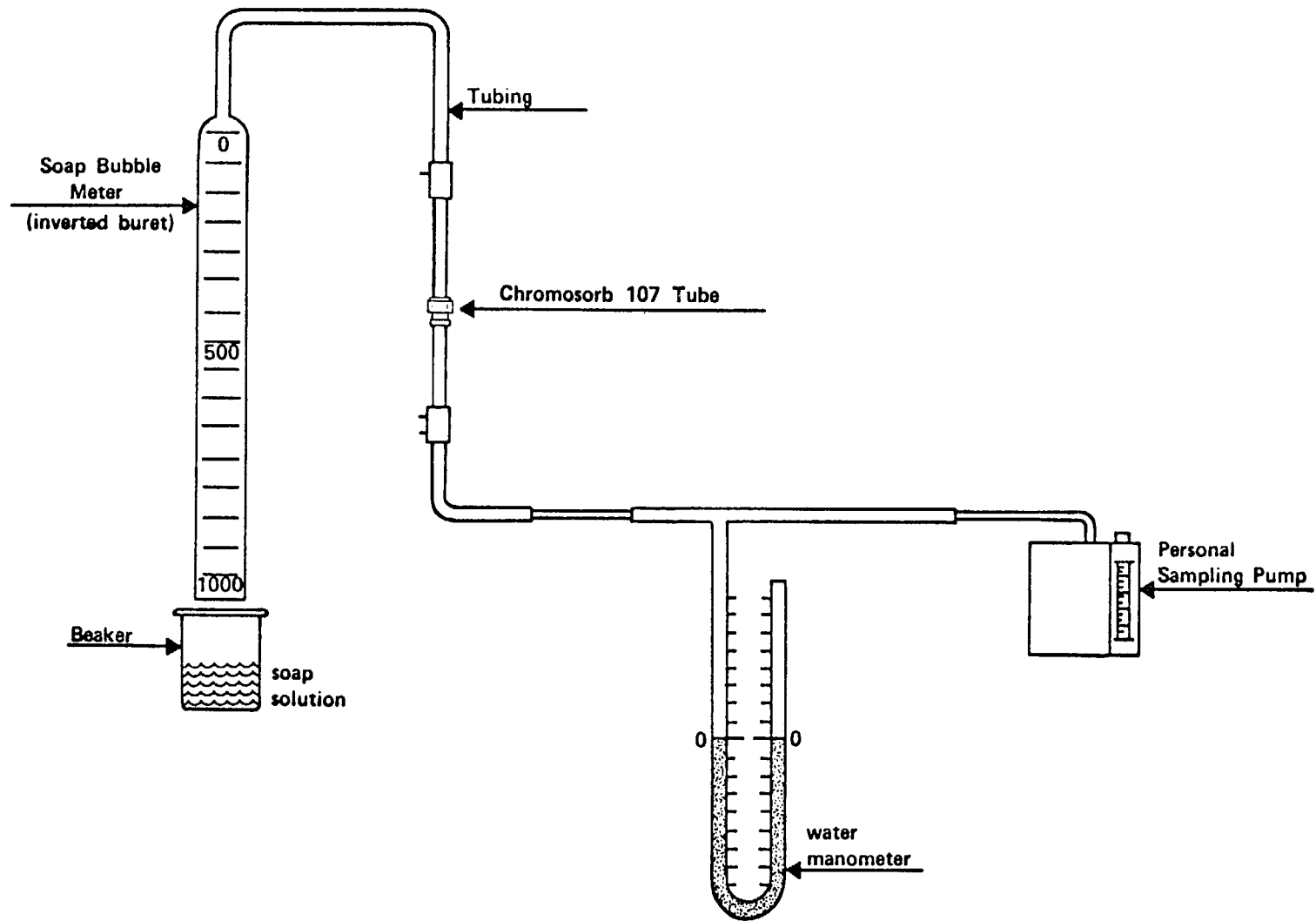


FIGURE XI-2

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH CHROMOSORB 107 TUBE

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HEALTH, EDUCATION, AND WELFARE  
PUBLIC HEALTH SERVICE  
CENTER FOR DISEASE CONTROL  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
ROBERT A. TAFT LABORATORIES  
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