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Standard Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes Use of Detector Tubes in the Measurement of Toxic Gases and Vapors¹

This standard is issued under the fixed designation D4490; 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 covers the detection and measurement of concentrations of toxic gases or vapors using detector tubes (1, 2).² A list of some of the gases and vapors that can be detected by this practice, their 1994–95 TLV values recommended by the ACGIH, practice and their measurement ranges are provided in Annex A1. This list is given as a guide and should be considered neither absolute nor complete.
- 1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.3 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.
- 1.4 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.
- 2. Referenced Documents as / catalog/standards/sist/ehc&ahah_767_47d1_&c32_4ad2&eeaea92/astm_d4490_23
- 2.1 ASTM Standards:³

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

2.2 Other Document:Documents:

29 CFR 1910 Federal Occupational Safety and Health Standard Title 29⁴

ISO 13137 Workplace Atmospheres – Pumps for Personal Sampling of Chemical and Biological Agents – Requirements and Test Methods⁵

3. Terminology

3.1 For definitions of terms used in this method, refer to Terminology D1356.

¹ This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality. Current edition approved Oct. 1, 2016March 1, 2023. Published October 2016April 2023. Originally approved in 1985. Last previous edition approved in 20112016 as D4490 – 96 (2011).(2016). DOI: 10.1520/D4490-96R16.10.1520/D4490-23.

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

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Code of Federal Regulations, Part 1910.1000 Subpart 2 and Part 1926.55 Subpart D.

⁵ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.



4. Summary of Practice (3)

- 4.1 Detector tubes may be used for either short-term sampling (grab sampling; $\frac{1}{2}$ min to 10 min typically) or long term sampling (actively or passively; $\frac{1}{2}$ h to 8 h) of atmospheres containing toxic gases or vapors.
- 4.1.1 Short-Term Sampling (Grab Sampling) (4-18)—A given volume of air (specified by the manufacturer) is pulled through the tube by a mechanical pump. If the substance for which the detector tube was designed is present, the indicator chemical in the tube will change color (stain). The concentration of the gas or vapor may be estimated by either (pump also specified by the manufacturer in a time period on the order of 1 min to 10 min. The length-of-stain is related to the amount of air sampled and the contaminant concentration during the sample period. For most detector tubes the concentration is determined by interpreting a) the length-of-stain compared to a calibration chart, or (the length of color change compared to the calibration curve affixed tob) the intensity of the the glass tube. There are some detector tubes which rely on the interpretation of the intensity of a color change compared to a set of standards color standard or standards provided by the manufacturers. The resultant color reaction may change over time and must be evaluated immediately by the user.
- 4.1.2 Long-Term Active Sampling (Long-Term Tubes) (19-22)—A sample is pulled through the detector tube at a slow, constant flow rate by an electrical pump. The time-weighted average concentration of the gas or vapor is determined by correlating the time of sampling either with (specified by the manufacturer by a pump over a 1 h to 8 h period. The length of color change and the sampling time are used a) the length-of-stain read directly from the calibration curve imprinted on the tube or (to determine the time weighted average (TWA) concentrationb) the intensity of the color change compared to a set of standards, of the contaminant.
- 4.1.3 <u>Long-Term Passive Sampling (Diffusion or Dosimeter Tubes) Length-of-Stain Dosimeter Tubes</u> (23)—The contaminant molecules move into the tube according to Fick's First Law of Diffusion. The driving force is the concentration differential between the ambient air and the inside of the tube. The time-weighted average concentration of the gas or vapor is determined by dividing the indication on the tube by the number of hours sampled (1-(typically 1 h to 10 h according to the manufacturers' manufacturer's instructions).
- 4.2 Instructions are given for the calibration of the sampling pumps required in this practice.
- 4.3 Information on the correct use of the detector tubes is presented.

5. Significance and Use

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- 5.1 The Federal Occupational Safety and Health Administration, in 29 CFR 1910, designates that certain gases and vapors must not be present in workplace atmospheres at concentrations above specific values.
- 5.2 This practice will provide a means for the determination of airborne concentrations of certain gases and vapors given in 29 CFR 1910.
- 5.3 A partial list of chemicals for which this practice is applicable is presented in Annex A1.
- 5.4 This practice also provides for the sampling of gaseous atmospheres to be used for process control or other purposes (2, 24-23).
- 5.5 Advantages of the Detector Tube Method:
- 5.5.1 As the detector tube method requires no chemical analyzers, external reagents, etc., advance preparations are not needed; detector tubes are always ready for use.
- 5.5.2 The detector tube method is well-suited for use at the work site because it is small, lightweight, and needs only a small sample volume to determine the concentration of gas or vapor in a sample.
- 5.5.3 The operating procedures are simple.
- 5.5.4 The results of measurements are available in just minutes, so fast action can be taken when needed.
- 5.5.5 Where no electrical power source is required, detector tubes can be used even when flammable gases are present.



- 5.5.6 Different types of detector tubes are available for different gases and measuring ranges, from 0.01 ppm to more than 10 %, depending on analyte and tube design, making the system flexible tor different sampling situations.
- 6. Interferences (26, 27)
- 6.1 Some common interferences for the various tubes are listed in the instruction sheets provided by the manufacturers.
- **6.** Apparatus and Operation (28-26-3129)
- 6.1 General—Short-term detector tubes are used for grab-sampling, capturing a concentration in a defined moment in time. They allow for the determination of contaminant concentrations, typically in the period of 1 min to 10 min with most measurements under 5 min.
- 6.2 *Apparatus*:
- 6.2.1 The detector tube method is a two-component system comprised of the detector tubes and pump(s) calibrated as a unit by the manufacturers. Detector tubes made by one manufacturer must not be used with pumps made by a different manufacturer due to the flow characteristics and physical relationship of the detector tubes and pumps.
- 6.2.2 In some sampling situations, particularly when testing for hazardous contaminant concentrations in confined spaces, a remote sampling line and adapter can be used. This allows placement of the detector tube in the potentially hazardous area to be tested while the operator is in a safer area (for example, sampling from a confined space prior to entry).
- 6.3 Detector Tube—A detector tube consists of a glass tube containing an inert granular material that has been impregnated with a chemical system which reacts with the gas or vapor of interest. As a result of this reaction, the impregnated chemical changes color. The granular material is held in place within the glass tube by porous plugs of a suitable inert material. The ends of the glass tube are flame-sealed to protect the contents during storage.
- 6.4 *Pump*-Pumped Systems (**3230**):
- 6.4.1 Short-Term Sampling—A mechanical, hand-operated, aspirating pump is used to draw the sample through the detector tube during the short-term sampling. Two types of pumps are commercially available: piston-operated and bellows-operated. The pumps have a capacity of 100 mL for a full pump stroke. stroke, and offer an option for collection of 50 mL. By varying the number of pump strokes, the sample volume is controlled. Sampling pumps should The pumps contain a flow-finish indicator that alerts the user to sampling completion. Sampling pumps shall be maintained and ealibration—the sampling volume checked periodically according to the manufacturer's instructions. The pumps shall be accurate to ± 5 % of the volume stated.
- 6.4.2 Long-Term Sampling—Small electrical pumps having stable low flow rates (2(2 mL/min) to 50 mL/min), are required for long-term sampling (2 to 8 h). sampling. Flow rates to be used with each detector tube are given by the manufacturers. As with the mechanical pumps, the electrical pumps mustshall be maintained and ealibrated the flow checked regularly. Maintenance and ealibration flow determination are performed using the instructions supplied by the manufacturer of the pump. The pump flow rate, and, therefore, the sampled volume, shall be accurate to $\pm 5\%$ of the stated flow rate. With this system either area or personal monitoring can be accomplished.
- 6.5 Diffusive Systems—Unlike pumped systems, neither a mechanical nor electric pump is required. Measurement is initiated as soon as the sampling end is broken, and is completed when re-sealed. Tubes are typically calibrated in terms of ppm.hours, where the reading is divided by the number of hours to provide the time-weighted average concentration in ppm. Because the diffusion coefficient (a component of Fick's Law) is affected by both pressure and temperature, corrections for these are required for accurate results.
- 6.6 Accessories—Several accessories are provided with detector tubes for special applications:
- 6.6.1 *Reactor Tubes*—These are tubes that are used in conjunction with detector tubes. Some gases and vapors, because of their low reactivity, are not easily detected by detector tubes alone. The reactor tubes consist of very powerful chemical reactants, which



break down the unreactive compound into other more readily detectable substances, which standard detector tubes can detect. Thus, the reactor tube is placed upstream of the detector tube and the combination must be used for certain compounds as a detector tube system.

- 6.6.2 *Dryer Tubes*—Water vapor interferes with the detection of certain substances; therefore, dryer tubes are used upstream of the detector tube in these cases as a pretreatment dehumidifier to remove the water vapor.
- 6.6.3 *Pyrolyzer*—A pyrolyzer is a hot wire instrument operated by batteries. Instructions for its use and maintenance are given in the manufacturers' instruction manuals. The purpose of the pyrolyzer, as with reactor tubes, is to break down difficult-to-detect compounds into other compounds more easily detected. The breakdown in this case is caused by heat. The pyrolzyer is particularly useful for organic nitrogen compounds, one of the products of breakdown being nitrogen dioxide, which is easily monitored.
- 6.6.4 *Remote Sampling Line*—When the sampling point is remote from the pump location, a length of nonreactive tubing can be attached to the pump with the detector tube attached to the other end of the tubing. This is useful for sampling in inaccessible or dangerous places.
- 6.6.5 Cooling Unit—The cooling unit consists of a length of metal tubing through which the sampled gas is pulled. Because of the high thermal conductivity of the metal tubing, the hot sampling gas is cooled sufficiently so that it will not destroy the indicator in the detector tube. The cooling unit must be placed upstream from the detector tube. Cooling units are particularly useful when sampling flue gases.
- 6.6.6 *Pipeline Sampling Kit*—The pipeline sampling kit provides representative gas and vapor sampling from pressurized systems. Made of chemically resistant materials, the sampler design allows the user to draw a detector tube sample from the center of the flow-through chamber. Ambient air cannot dilute the sample as long as a positive flow is maintained.
- 6.6.7 Personal Sampling Pump—When using long-term pumped tubes (6.4.2) a sampling pump is required. The pump should meet the specifications of ISO 13137 and have its flow rate set and verified in accordance with Practice D5337 before and after sampling.
- 6.6.8 Sample Holder—To be used with long term pumped tubes or diffusive tubes to attach the tube to the person whose breathing air is being sampled.

7. Procedure

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- 7.1 Detector tubes made by one manufacturer must not be used with pumps made by a different manufacturer (31). Each lot of detector tubes is calibrated at the manufacturer's plant, using their equipment. The pumps of other manufacturers have different flow characteristics that cause different lengths-of-stain, resulting in erroneous readings.
- 7.2 Use of detector tubes should be conducted under the supervision of a trained professional such as a chemist or an industrial hygienist. Carefully follow the instruction sheet of the manufacturer for the proper use of each detector tube. Check the pump for leaks, total volume, and flow rate in accordance with the instruction manual for the pump. Also check the sampling line for leaks (if used).
- 7.3 Remove one detector tube from the box and break off both tips for pumped tubes or the sampling end of a diffusive tube.
- 7.3.1 For pumped tubes, insert the detector tube into the pump inlet or onto the sample line, making sure that it is properly oriented with the arrow pointed toward the pump inlet. For some chemicals, reactor tubes (6.6.1) or dryer tubes (6.6.2) may need to be added in front of the detector tube as part of the sampling train. Other methods may require the use of a pyrolyzer (6.6.3).
- 7.3.1.1 Face the mounted detector tube into the atmosphere to be tested. Sample an appropriate volume of air by pulling the pump handle out for the required number of strokes if using a piston pump, or squeezing the pump the proper number of times if using a bellows-type or bulb-type pump, or if using a long-term pumped detector tube, attaching the personal sampling pump and tube in a holder (6.6.8) to the person whose breathing air is being sampled and switching on the pump. Consult the manufacturer's instruction sheet on how much volume is required for your desired sampling range (8.2).
- 7.3.1.2 Allow the sample volume to pass through the tube as indicated by pump's flow-through indicator or switch off the personal sampling pump after the desired sampling interval and calculate the volume passed. Wait the specified time as directed on the tube instruction sheet prior to reading the length-of-stain.

- 7.3.1.3 If the contaminant is present, the indicator chemical in the tube will change color (refer to the instruction sheet). The length of stain, correlated with the volume of air sampled, will indicate the concentration. Most detector tubes now have direct reading concentration scales printed on the tube.
- 7.3.2 For diffusion tubes, insert the tube into its holder (6.6.8) and attach to the person whose breathing air is being sampled. Record the time of the commencement of sampling and record the time when sampling is finished. The time elapsed can be used with the scale to calculate the concentration. Temperature and pressure corrections may be necessary (6.5).
- 7.4 Detector tubes use chemical reagents that inevitably deteriorate over time. Because of this, if detector tubes are used after the stated shelf life expiration date (stamped on each box of tubes), they may not show an accurate gas or vapor concentration
- 7.5 Detector tubes should be stored in a cool, dark place to ensure adequate shelf life, that is, at a temperature of 25 °C or less and out of direct sunshine even if a specific temperature is not shown on a box. Detector tubes stored at high temperatures or in direct sunlight may show deterioration in performance even if they are within the stated shelf life. Some detector tubes are required to be stored under refrigeration until use at a temperature between 0 °C and 10 °C or as otherwise stated on the box.

8. Conditions That Affect Detector Tube Results

- 8.1 Interferences and Cross Sensitivity—Virtually all methods of gas and vapor detection (detector tubes, electrochemical sensors, PIDs) must cope with the potential interference by other contaminants present in the atmosphere being tested. The following are some common examples particular to detector tubes. It is not the intent of this subsection to elaborate all possible scenarios. Some common interferences and cross sensitivities for the various tubes are listed in the instruction sheets provided by the manufacturers. Significant interferences have been the subject of study (32, 33). The following are consequences and results from potential interference by other contaminants:
- 8.1.1 The indication is not affected by other gases and vapors.
- 8.1.2 The indicating layer can react with other gases and vapors to produce a color change, but the interfering components are retained in a prelayer ahead of the indication layer. The interferent may produce a color change in the prelayer, but this is not always the case.
- 8.1.3 The indication layer reacts with several gases and vapors; it is not possible to incorporate a prelayer to trap these other gases and vapors.
- 8.1.4 The other gases and vapors present in the air react with each other. The reaction can happen when the molecules of these gases and vapors are concentrated on the reagent in the detector tube. The filling in the detector tube catalytically accelerates such reactions.
- 8.1.5 The other gases or vapors are converted to a new chemical compound by the prelayer. The prelayer is designed to convert the target contaminant, but also converts other gases and vapors of similar chemical characteristics.
- Note 1—It is important for the user to review available literature from the manufacturers such as the instruction sheets included in the package, detector tube handbooks, and online information published by the manufacturers. The manufacturers can also be contacted directly for application support.
- 8.2 Sample Volume—Graduations on the mechanically pumped detector tubes showing the concentration of gas are generally calibrated to 100 mL (100 cm³) per stroke, more or less, the quantity of gas passed through the detector tube being determined by the manufacturer's pump type and stroke count. The term pump "stroke" simply means the number of times the sample pump is operated. For long-term pumped detector tubes the sample volume is the average of the flow rate set at the beginning and end of sampling divided by the time of sampling. Diffusive detector tubes do not have a sample volume.
- 8.2.1 The discolored layer generally lengthens in proportion to the quantity of gas or vapor passed through the detector tube. When a gas or vapor is present in concentrations lower than the lowest graduation on the detector tube, the approximate concentration value can be found by increasing the sample volume to several hundred mL (that is, several pump strokes) and dividing the concentration value read on the detector tube by the number of pump strokes. It should be noted, however, that the quantity of gas or vapor detected may not be exactly proportional to the length of the discolored layer obtained due, for example, to the effects of moisture or a depleted oxidizer.

- 8.3 *Temperature*—The temperature of the gas detector tube (normally the same temperature in the sampling environment) can also affect the measured concentration of gas or vapor for the following reasons: (1) an increase or decrease in the sample volume caused by a temperature change; (2) a change in the quantity of gas adsorbed by the detecting reagent; (3) a change in the rate in which the detecting reagent reacts with the gas or vapor; (4) for diffusive tubes, a change in the diffusion coefficient (6.5) which is also affected by changes in pressure.
- 8.3.1 These effects can overlap one another, causing the length of the stain in the detector tube to increase or decrease, or they can offset one another, having no effect on the measured value. Those gas detector tubes that can be affected by temperature changes are provided with a temperature correction table as part of the instruction sheet which is packed with each box of detector tubes.
- 8.4 Humidity—While nearly all detector tubes are not affected by atmospheres unsaturated with respect to water vapor, some detector tubes are formulated with either a dehumidifying reagent and detection reagent together in tube, or a separate dehumidifying tube that is connected to the detector tube with a connector supplied in each box of tubes. However, water droplets can enter a detector tube and water can even condense inside the detector tube due to temperature changes. Both these situations can have a serious effect on both the gas or vapor readings obtained and the actual colour change of the detector tube. For these reasons, taking humidity readings prior to gas or vapor sampling is recommended.
- 8.5 Coexisting Gases or Vapors—While the detecting reagents in detector tubes are formulated to react with the gas or vapor to be measured, they can also show a similar reaction (colour change) with another gas or vapor (or gases or vapors) having similar chemical properties. It is necessary to carefully consider this when taking gas or vapor readings with any detector tube. A coexisting gas or vapor can have the following effects on detector tubes: (1) it may not discolor the detecting reagent, but can give a higher or lower reading; (2) it can discolor the detecting reagent in a similar way, giving a higher reading than the actual concentration; (3) it can give an entirely different colour change in the tube; (4) it can give the discolored length with an indistinct end point.
- 8.6 Reaction Rate—With most detector tubes the reaction rate is fast and the length of stain is proportional to the product of the concentration and sampled volume. In these cases the reading can be extrapolated linearly between gradations (for example, the half-way point between 100 ppm and 200 ppm would be 150 ppm). However, there is a subset of tubes where the reaction rate is slow and proportional to the logarithm of the product of concentration and volume, in which case the extrapolation between gradations is not linear. Care must be taken to consult the manufacturers' directions when extrapolating readings.
- 9. Reagents/standards.iteh.ai/catalog/standards/sist/ebc8abab-7ff2-42d1-8c32-4ad28eeaea92/astm-d4490-23
- 9.1 The reagents used are specific for each tube, and, to detect a specific gas, may vary from manufacturer to manufacturer. Detector tube chemistry is typically based on acid-base, oxidation, reduction, or precipitation reactions. The instruction sheets supplied by the manufacturers give the principal chemical reaction(s) that occur(s) in the tube, thus showing the reagent that is used to react with the gas or vapor to produce the color change.
- 9.2 The detecting reagent is a reactive chemical adsorbed by granules (the carrier) such as silica gel, activated alumina, silica sand, silica glass, or polymer beads. This packing changes color by the chemical reaction of the reagent with the target gas or vapor. Because of this, reactive reagents are selected to meet the following criteria: (1) the color-developing reagent should be stable when absorbed on the carrier and have a long shelf life; (2) the reagent should show a sharp color change reaction with the target gas or vapor and be acceptable in selectivity; (3) the detecting reagent should give a strong color contrast both before and after the color change reaction; (4) the detecting reagent should react with the target gas or vapor in the sample quickly and develop a discolored length with a clear end point.
- 9.3 Pre-layers are frequently included. There are three primary functions of the pre-layers: trap interfering gases and vapors, act as a desiccant, or chemically convert a gas or vapor to a chemical that will react in the indication layer.

9. Sampling with Detector Tubes

9.1 General—Detector tubes made by one manufacturer must not be used with pumps made by a different manufacturer (33). Each lot of detector tubes is calibrated at the manufacturer's plant, using their equipment. The pumps of other manufacturers have different flow characteristics that cause different lengths-of-stain, resulting in erroneous readings.

9.2 Procedure (34)—The detector tube program should be conducted under the supervision of a trained professional such as a chemist or an industrial hygienist. Carefully follow the instruction sheet of the manufacturer for the proper use of each detector tube. In general, the instruction sheet will include the following information.

- 9.2.1 Storage conditions.
- 9.2.2 Shelf life.
- 9.2.3 Chemical reaction and color change.
- 9.2.4 Test procedure.
- 9.2.5 Significant interferences.
- 9.2.6 Temperature and humidity correction factors, if required.
- 9.2.7 Correction for atmospheric pressure.
- 9.2.8 Measurement range.

10. Accuracy of Detector Tubes

10.1 The Safety Equipment Institute (SEI) has a certification program for certain detector tubes used in short-term sampling. This program is similar to the NIOSH program for evaluating and certifying detector tube performance (35, 36). Under this program, the tubes are required to meet an accuracy (95 % confidence level) of ±25 % between one and five times the SEI test concentration and ±35 % at one half the test concentration. The SEI test concentration is chosen as the Threshold Limit Value as defined by the American Conference of Governmental Industrial Hygienists for the test gas or vapor (37). The calculation of tube accuracy is based on a set of statistical procedures (38) and provides an estimate of accuracy under actual use conditions. The SEI Certified Equipment List should be consulted for the listing of approved units.

10.1 In general, the accuracy of any detector tube depends on the construction and chemistry of the tube along with the actual composition of the test atmosphere and the conditions under which the tube is read. For gases and vapors not covered by the SEI program, detector tubes may or may not meet the accuracy requirements of the previous paragraph The manufacturers of detector tubes state accuracies over a range of $\pm 5\%$ to $\pm 40\%$ in the instructions for use included in the packages or the detector tube handbooks, or both. The best accuracy statements for detector tubes are $\pm 5\%$, the majority are in the range of $(\pm 10\%$ to 39, $\pm 15\%$ There is also some variation in accuracy between manufacturers' tubes designed to detect a specific compound. Therefore the user should verify the accuracy with the tube manufacturer or run his own tests to determine accuracy and others, which are the exceptions, are $\pm 40\%$. Nevertheless, this information is provided by the manufacturers and the user (41-43). It must be emphasized that a correct estimate of accuracy can only be done by qualified operators and with careful attention to the generation and verification of test gas or vapor concentrations can make an informed decision. (44).

10.2 Because the accuracy of a detector tube in sampling a specific compound depends on the cross-sensitivity of the tube to other gases or vapors present in the test atmosphere, the manufacturer should be consulted for information on cross-sensitivity effects for the specific chemistry employed in their tube. Quite frequently, several different indicating chemistries for a Ideally the accuracy should be within $\pm 25\%$ for measurements spanning $0.5\times$ to $2\times$ the applicable occupational exposure limit, and at one time this was assessed through certification programs **specific**(34, 35compound), are available. Proper choice of indicating chemistry can minimize the effect of a co-contaminant in the test atmosphere but these are no longer in effect.

11. Keywords

11.1 air monitoring; detector tubes; dosimeter sampling; grab sampling; sampling and analysis; toxic gases and vapor; vapors; workplace atmospheres