CHAPTER 11
DETECTOR/DIFFUSION TUBE SAMPLING

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I.   Introduction

Ambient air contains about 78% nitrogen, 21% oxygen, 0.04% (400 ppm) carbon dioxide, and small amounts of argon, helium, and other gases. If the concentrations of these gases change due to the addition of another gas, the potential for adverse health effects exists.

The list of other gases that might be present is extremely broad and the associated hazard of each varies considerably. The contaminant, its concentration, duration of exposure, and additive effects with other gases must all be considered. Although some gases have odors, the odors may not be detectable at concentrations below the exposure limits.

If there is a suspected hazard, the air should be tested to determine the substance that caused the change. To determine the hazard potential of a gas, it is necessary to measure its concentration. Detector tubes can be used for instantaneous measurements of approximately 350 different gases and vapors. Diffusion tubes can be used for full-shift sampling of approximately 20 of these contaminants.

II.   Definitions

Detector tubes - small glass tubes with both ends flame-sealed which contain reagent chemicals. When the ends are broken and contaminated air is drawn through the tube, the reagent chemicals react with the gas or vapor to produce a color change (stain). The color change varies in length in proportion to the concentration of the contaminant.

Diffusion - the natural passage of gas or vapor from an area of high concentration to an area of lower concentration. When gases or vapor pass through a membrane, the rate of diffusion depends on the concentration of contaminants on each side of the membrane. In a diffusion tube, the gases or vapors will diffuse through the reagent chemical contained in the tube and cause a color change which corresponds to a time-dependent concentration.

Diffusion tube - a specialized detector tube that can be used as a passive monitor for long-term sampling of mine gases and vapors. The contaminants sampled enter the tube by natural diffusion of air. As gases or vapors diffuse through the tube, the chemicals within will react and produce a color change or stain which varies in length according to the concentration. Diffusion tubes are typically used during a work shift of up to eight

hours, but can be used to determine average concentrations over periods of several hours. Follow the manufacturer's instructions provided with each box of tubes.

Grab sample - a term used to describe a sample taken in a short period of time to assess the concentration of a given contaminant (e.g., detector tube sample).

III.   Exposure Limits

The full-shift threshold limit values (TLVs®), Ceiling and Excursion limits, and the short-term exposure limits (STELs) for contaminants sampled with detector tubes and diffusion tubes are listed or referenced in the ***TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1973***. They are incorporated by reference in MSHA standards (30 CFR §§ 56/57.5001). For the appropriate selection of different tubes and the respective exposure limits for specific contaminants, refer to Chapter 3.

IV.   Equipment Factors and Environmental Corrections

Many variables can affect the measurement accuracy of detector and diffusion tubes and must be carefully controlled.

   A.   **Shelf Life** - All detector (short-term) and diffusion (long-term) tubes have a shelf life that is normally noted on the box or on the sampler itself. Do not use tubes for enforcement sampling after their shelf life expires. Do not re-use tubes.

   B.   **Storage** - Specific instructions for tube storage are printed on the tube box or in the instructions. Refrigeration is recommended, but is not necessary. Some tubes must be protected from freezing temperatures, and others from extended periods of time at temperatures above 85° F (30° C). Always check for the manufacturer's storage instructions and recommended ambient operating conditions.

   C.   **Temperature and Humidity** - Use a sling psychrometer or a digital thermometer / hygrometer to determine temperature and humidity conditions. Record these readings in the Health Field Notes. Corrections for temperature or humidity are a function of each particular tube. Read the instructions which come with each set of tubes to determine the appropriate correction factors for that tube. Do not use tubes outside the recommended temperature or humidity range without using correction factors. Normally, if sampling is done between 50° F and 85° F (10° C to 30° C), and below 65% humidity, no correction factors are necessary. If

sampling conditions are outside the manufacturer's specified limits, contact your District Office for guidance.

Moisture (steam, rain, snow, mist, or fog) can reduce collection efficiency by saturating the tube and interfering with the collection of the contaminant. Check the manufacturer's instructions for use and plan your sampling accordingly.

D.   **Interferences** - Sampling may be adversely affected when other gases or vapors are present because these gases or vapors can react with the reagent chemicals inside the detector or diffusion tube. Refer to the instructions inside each box of tubes to ensure that your sampling result shows only the contaminant you intend to measure.

For example: a certain tube measuring carbon monoxide becomes inaccurate when hydrogen sulfide is present. If hydrogen sulfide may be present, use a tube that isn't affected by hydrogen sulfide or use another means of sampling. Contact your District Office for guidance.

E.   **Tube reading** - Watch the length of color change in the tube's indicating layer. Any departure from a sharp demarcation between the reacted chemical and the un-reacted chemical in the tube is the "indicating layer." Read the stain length from the zero point to the best estimate of the end point of this layer. Take special care to note the units for tubes marked with concentration gradations. Some are marked in percent and some in ppm, depending on the concentration range to be measured.

Note: Some detector tubes are marked with two scales, dependent on the number of strokes taken. Use the appropriate scale when reading the tube.

If multiple stains occur in the tube, it is an indication of the presence of interfering contaminants, and the tube cannot be used for compliance. Caution: do not mistake normal color gradations with multiple stains. Multiple stains vary appreciably in both color and end point and may be separated by uncolored areas between the multiple end points.

F.   **Error Factor** - The sampling factors needed to determine compliance when using detector or diffusion tubes vary and can be found in Chapter 3.

G. **Correction Factors for Elevation** - Elevation changes relative to sea level affect tube accuracy because they affect the density of the air being drawn or diffused through the tube. Make appropriate corrections for elevation to detector and diffusion tube readings by multiplying the concentration indicated on the tube by the correction factors given in Figure 11-1.

Figure 11-1. Elevation Correction Table for Detector and Diffusion Tubes

Elevation in feet (meters)	Correction Factor	Elevation in feet (meters)	Correction Factor	Elevation in feet (meters)	Correction Factor
-5000 (-1524)	0.83	500 (152)	1.02	7000 (2134)	1.31
-4500 (-1372)	0.85	1000 (305)	1.04	8000 (2438)	1.36
-4000 (-1219)	0.86	1500 (457)	1.06	9000 (2743)	1.41
-3500 (-1067)	0.88	2000 (610)	1.08	10000 (3048)	1.46
-3000 (-914)	0.90	2500 (762)	1.10	11000 (3353)	1.52
-2500 (-762)	0.91	3000 (914)	1.12	12000 (3658)	1.58
-2000 (-610)	0.93	3500 (1067)	1.14	13000 (3962)	1.64
-1500 (-457)	0.95	4000 (1219)	1.16	14000 (4267)	1.71
-1000 (-305)	0.96	4500 (1372)	1.18	15000 (4572)	1.77
-500 (-152)	0.98	5000 (1524)	1.21	---	---
0 (sea level)	1.00	6000 (1829)	1.26	---	---

V.   Sampling Strategy

   A.   Full-Shift Samples

Full-shift sampling using detector or diffusion tubes should be used when miners may be exposed to gases or vapors during their scheduled workshift and to determine if TLV®'s have been exceeded. Always follow the manufacturer's guidelines for sampling times and concentration ranges. If the shift extends beyond 8 hours, the tube may need to be changed.   Refer to Chapter 3 for TLV®s and specific sampling guidelines for individual contaminants. The full-shift samples should be supplemented with grab samples (detector tube, TMX-412 readings, or other electronic direct-reading instruments) for persons of the same occupation taken throughout the shift to corroborate the full-shift data. The grab samples also serve as "stand-alone" short-term samples for compliance with the associated short-term exposure limits (STELs). If, in the midst of full-shift sampling, an individual grab sample exceeds the STEL for an individual gas, that sample can stand alone for citing an overexposure based on exceeding a short-term limit.

Since diffusion tubes are not available for many contaminants found in the mine environment, full-shift compliance determinations must be made using other means. For contaminants which can be assessed by using detector tubes, full-shift sampling can be accomplished using partial-period sampling by taking a series of grab samples spaced periodically throughout the shift. Each such grab sample serves the dual purpose of being part of the full-shift sampling process as well as being a stand-alone short-term sample. See Chapter 2 for calculating full-shift exposure from partial-period data.

   B.   Short-Term Grab Samples

Short-term samples can be taken independently with calibrated detector tube pumps or electronic direct-reading instruments (e.g., TMX-412) to determine if short-term exposure limits (STEL), excursion limits, or ceiling limits have been exceeded during suspected periods of peak exposure. When monitoring for short-term exposure limits, refer to the sampling times in Chapter 3.

Note: Short-term samples should be taken in conjunction with full-shift samples to corroborate the full-shift data.

VI.   Diffusion Tube Sampling Procedures

Diffusion tubes are specialized detector tubes that are used as long-term monitors for 8 - 12 hours. For workshifts longer than 8 – 12 hours use consecutive tubes. The gas being sampled enters the tube by natural diffusion of air (no pump is required). The gas reacts with the chemical reagents within the tube to produce a color change. These tubes can be used as full-shift personal samples, with the full-shift exposure being calculated (the direct reading divided by the time in hours) at the end of the shift. Diffusion tubes are available for several contaminants commonly found in the mining environment, such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and hydrocyanic acid (HCN).

A.   Preparing the Tube
The diffusion tube has a breaking bead designated by a "red" dot. Wait until you are ready to sample before breaking the tube, then, following the manufacturer's instructions, break the tube and place it in the associated holder. Push the half of the tube that has the indicating layer as far as it will go in the direction of the arrow into the top part of the holder. Fold the bottom part of the holder around the tube and click it in place. Push the tube down until the glass rim of the open end rests against the bottom part of the tube holder (see Figure 11-2).
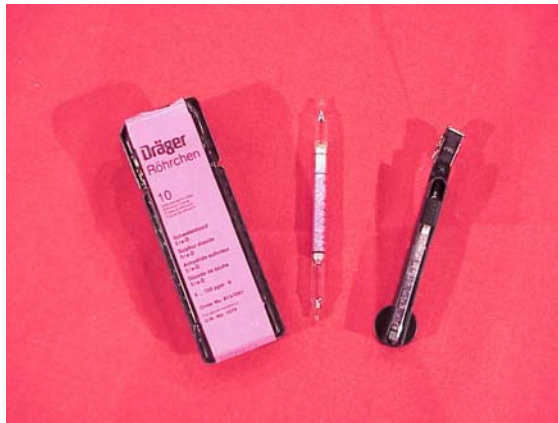
B.   Positioning the Holder

Figure 11-2. Diffusion Tube and Holder

Clip the tube holder(s) to the miner's clothing within the breathing zone. When properly assembled and attached, the open side of the tube should point downward. If the miner is not wearing a shirt, the inspector should provide a vest to facilitate sampling. Vests can be obtained through the District Office.

C.   **Instructions to the Miner**

    1.   Explain to the miner what you are doing, what the sampling device does, and the reason for the sampling (*i.e.*, the hazard). If available, issue a Miner Health Hazard Information Sheet or Card.

    2.   Instruct the miner not to remove the diffusion tube at any time or cover it with a coat or anything else. If the miner must leave the mine property or work area during the shift, the inspector should remove the diffusion tube and immediately record the direct-reading ("detector tube indication") and sampling time. When the miner returns, resume sampling with a new diffusion tube.

    3.   Instruct the miner not to abuse or tamper with the diffusion tube.

    4.   Emphasize the need for the miner to continue to work in a routine manner and report to you any unusual occurrences during the sampling period.

    5.   Inform the miner when and where you will remove the diffusion tube and that you will be checking the tube throughout the shift.

D.   **Collect the Sample**

    1.   When the diffusion tube holder has been attached, record in the Health Field Notes the following:

- The contaminant being sampled;
- Time the tube was opened and attached;
- Miner's name, job title, and work location(s);
- Shift hours per day and days per week worked;
- Expiration date of the tube and ID number; and
- Elevation of the sampling site.

    2.   During each full-shift sample, the inspector must observe the miner being sampled as frequently as is necessary to determine that a representative sample is being conducted of the normal activities. Check the condition and positioning of the diffusion tube. Record what tasks the miner has performed in the time between subsequent checks, so that the completed Health Field Notes will describe the miner's full work shift. This requirement does not necessarily preclude the inspector from doing other inspection work while sampling.

3.   Throughout the shift, record any other pertinent information in the Health Field Notes, such as:

- Times that the diffusion tube was checked. If the tube needs to be removed or replaced for any reason, record the times involved.
- Controls in use with general description and whether or not they seem adequate.
- Potential sources of exposure, a general description of these sources, number of persons affected, and possible additional control measures.
- Activity of miner, equipment operating in the area, and approximate time spent at each activity.
- Any other samples taken (e.g., detector tubes, badges, noise, etc.) and results, if available.
- For any consecutive samples taken, the direct-readings and sampling times for any additional tubes used during sampling period.
- Environmental conditions (such as wind conditions, temperature, humidity, ventilation, etc.).

4.   Collect the diffusion tube and holder from the miner. Immediately record the ending time. Read the tube, determine the test result and record it.

VII.   Detector Tube Sampling Procedure

Detector tubes are small glass tubes which contain reagent chemicals. Both ends are flame-sealed. When the ends are broken and contaminated air is drawn through the tube, the reagent chemicals react with the gas or vapor to produce a color change (stain). These color changes vary in length according to the contaminant concentration.

A.   Detector Tube Pump System

A detector tube and bellows-type sampling pump are used together to form a direct-reading sampling system (see Figure 11-3). This system is used to determine the short-term concentration of gases or vapors in the air. Several manufacturers are marketing pump-tube systems for measuring a wide variety of contaminants. Each manufacturer has specific instructions which apply only to that particular pump-tube system. <u>Read, understand, and follow the manufacturer's instructions</u> for the pump-tube system you are using. Never interchange units or components from one pump-tube system to another.

Figure 11-3. Detector Tube and Bellows-Type Pump Systems

1.   **Bellows Pump Testing** - The length of color change on a detector tube is
        directly related to sample size. The hand-operated bellows pump supplies
        100 mL of sample with each full stroke. Any malfunction will result in
        less volume being pulled through the detector tube. Therefore, it is
        essential to check the volume drawn through the pump at least once a
        year. In addition, the bellows pump must be re-tested any time it has been
        repaired or disassembled for cleaning.

        Volume Test - A 100 mL glass burette or a digital sample pump calibrator
        can be used to check the volume pulled by the pump per stroke.

                •   Using a 100 mL glass burette or sample pump calibrator,
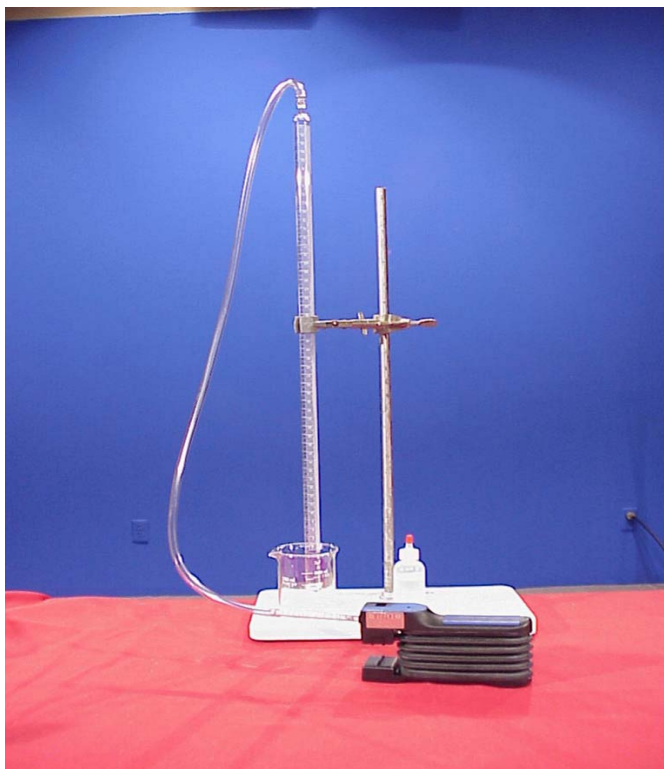   connect the apparatus as shown in Figure 11-4.

Figure 11-4. Assembly for Volumetric Testing of Bellows Pump

- Thoroughly wet the inside of the calibration burette or calibrator cylinder. Position a soap bubble at the zero mark of the burette or cylinder, using the pump to ease the bubble into position.
- Depress the bellows completely and release.
- Measure the volume of air pulled through the burette. Take several measurements to ensure that the reading is consistent.
- The pump must pull between 95 and 105 mL (±5 percent) for an acceptable test. If the pump pulls less than 95 mL or more than 105 mL, the pump must not be used before it is repaired.
- Record the pump ID number, volume (mL) pulled, date of testing, and initials of person performing calibration. Record this information on a gummed label and apply the label to the inside of the pump carrying case. An alternative is to record this information in a pump calibration log.

Leak Test - When a detector tube sample is taken with a bellows-type pump, the pump must be checked <u>before</u> and <u>after</u> <u>each</u> <u>survey</u> <u>shift</u> to ensure that the sample volume is drawn first through the tube and then through the bellows pump. Any leakage through the pump causes erroneous concentration values. To perform a leak test, follow this procedure:

- Insert an unbroken detector tube into the tube holder and completely compress the bellows.
- Wait 10 minutes. If the bellows pump remains compressed for the duration of the test period, assume no air leak.
- If there is leakage, the pump needs cleaning or repair. Do <u>not use it</u> for compliance determination.

Suction Test - To ensure that the bellows pump can draw air through the sample tube, perform the following <u>before</u> and <u>after</u> <u>each</u> <u>survey</u> <u>shift</u>:

- Compress the bellows pump completely.
- Release the pump - the bellows should instantly return to the starting position.
- If not, the pump needs cleaning or repair. <u>Do not use it</u> for compliance determination.

2.   **Sampling Time** - A definite period of time must elapse from the start of sampling to the time when the tube is read. This ensures that enough time has passed for the chemical reaction to take place between the tube ingredients and the contaminant.

The amount of air required (number of strokes), the waiting period between strokes, and the chemical reaction time vary with the individual type of tube, the tube manufacturer, and the concentration of the contaminant. Each box of tubes contains this information, which must be followed exactly.

B.   **Assess Sampling Conditions**

If required by the manufacturer's directions, use a sling psychrometer or a digital thermometer / hygrometer to take temperature and humidity measurements at the sampling site. Also, note the elevation of the site. Record all necessary information in the Health Field Notes.

C.   **Prepare Tube for Sampling**

1.   Select the appropriate tube for the measurement required, and note the number of strokes required, as specified in the instructions packed with the tubes.

2.   Open each end of the tube by using a tube breaker or by inserting the tip gently into the tube opener hole in the bellows pump. The openings should be approximately one-half the internal diameter of the tube.

3.   Insert the proper end of the detector tube into the tube holder of the pump. An arrow on the tube indicates the direction of air flow. Air to be sampled must not pass through any hose or tubing before entering the detector tube. Note: If the bellows pump is provided with a stroke counter, reset the counter before taking a sample.

D.   **Collecting a Grab Sample**

1.   **Instructions to the miner** - Explain to the miner what you are doing, what the sampling device does, and the reason for the sampling (*i.e.*, the hazard). If available, issue a Miner Health Hazard Information Sheet or Card. Emphasize the need for the miner to continue to work in a routine manner and report to you any unusual occurrences during the sampling period.

2.   **Procedure** - Position the detector tube in the breathing zone of the miner, taking care not to endanger the miner with the broken end of the tube. Take the required number of strokes to properly assess the gas concentration:

   •   Squeeze the pump completely, release it, and wait until the bellows pump fully expands. Note: when using a pump with a stroke counter, wait until the end-of-stroke indicator appears. If more than one stroke is needed, squeeze the pump completely again. Repeat until the number of strokes corresponds to that given in the tube instructions.
   •   In between samples, remove the tube from the socket, and flush bellows pump with a few pump strokes of clean air.

   Ceiling limit - take the required number of strokes on the detector tube and compare the reading with the ceiling limit concentration.

Short-term exposure limit (STEL) and excursion limit - determine the minimum time (refer to Chapter 3) allowed for the exposure limit of the gas or vapor you intend to measure. Use partial-period sampling by taking detector tube readings over this entire time period and calculate the average concentration.

Example: the short-term limit is for a 30-minute exposure:

- Take one tube reading during the first 5-minute period.
- Take the second tube reading midway through the 30-minute period.
- Take the third tube reading in the final 5-minute period.
- Add all three readings and average (divide by 3) to obtain the concentration of the short-term exposure.

Record the tube readings, calculations, and concentration in the Health Field Notes.

VIII.   Post-Inspection Procedures

A.   Review Health Field Notes

Check that you have recorded all necessary information in the Health Field Notes (MSHA Form 4000-31). Refer to Chapter 21, Section V.

B.   Post-Survey Leak Test of Bellows Pump (when using detector tubes)

After the survey, perform a leak test as described in Section IV.B.1 of this chapter. If the bellows pump fails the leak test, void the results of any grab samples taken.

IX.   Compliance Determination

A.   Diffusion Tubes

Determine compliance by comparing calculated exposure concentrations with respective enforcement exposure limits.

1. **Full-Shift Sample**: calculate the full-shift exposure using the following formula:

$$\text{SWA in ppm} = \frac{\text{Diffusion Tube reading in ppm·h}}{8 \text{ hours}}$$

where: h represents hours.

Example: The TLV® for sulfur dioxide (SO_2) is 5 ppm. An SO_2 sample is taken for 7 hours 30 minutes at sea level, and tube stain reaches the 50 ppm·h demarcation line.
At sea level, the correction factor is 1.00 (from Figure 11-1):
(50 ppm·h) X (1.00) = 50 ppm·h

$$\text{SWA} = \frac{50 \text{ ppm·h}}{8 \text{ hours}} = 6.25 \text{ ppm}$$

The error factor for Dräger SO_2 5/a-D diffusion tube # 8101091 is 1.41.
The full-shift enforcement TLV® = 1.41 x 5 ppm = 7.05 ppm.
The sample with the error factor applied indicates compliance.

2. **Consecutive Tube Sampling (Full-Shift longer than 8 hours)**: If the workshift is longer than 8 hours, use an additional diffusion tube. Each of the additional sampling periods must be 1 to 8 hours in duration. It may also be necessary to change tubes during a shift if the limit of the tube's capacity is approached. In either case, calculate the full-shift exposure using the following formula:

$$\text{SWA in ppm} = \frac{D_1 + D_2 + D_3 + \ldots + D_n}{8 \text{ hours}}$$

where: D = Diffusion Tube reading in ppm·h

Example: The TLV for carbon monoxide (CO) is 50 ppm. At 7:00 a.m., a CO diffusion tube_1 was placed on a miner working at a depth equal to 1500 feet below sea level. A spot check of the tube at approximately 11:00 a.m. indicated a reading of 200 ppm·h. At 12:00 p.m. the tube_1 read 300 ppm·h. This reading was recorded and a new CO tube_2 was placed in the holder. It was noted that a very smoky diesel-powered piece of equipment had begun operation in the area. At 1:00 p.m. the reading on the new tube_2 was 400 ppm·h. The reading was recorded and a new tube_3

was placed in the holder. By 7:00 p.m., the end of the shift, tube$_3$ read 300 ppm·h.

The three recorded tube readings require adjustment for elevation.

At -1500 feet, the correction factor is 0.95 (from Figure 11-1):

$$(300 \text{ ppm·h}) \text{ X } (0.95) = 285 \text{ ppm·h}$$
$$(400 \text{ ppm·h}) \text{ X } (0.95) = 380 \text{ ppm·h}$$
$$(300 \text{ ppm·h}) \text{ X } (0.95) = 285 \text{ ppm·h}$$

Apply compliance determination formula:

$$\text{SWA} = \frac{(285 \text{ ppm·h})_1 + (380 \text{ ppm·h})_2 + (285 \text{ ppm·h})_3}{8 \text{ hours}} = \frac{950 \text{ ppm·h}}{8 \text{ hours}} = 119 \text{ ppm}$$

The error factor for Dräger CO 50/a-D diffusion tube # 6733191 is 1.41.
The full shift enforcement TLV$^®$ is: 1.41 X 50 ppm = 70.5 ppm.
The sample indicates a citable overexposure has occurred.

B.   Detector Tubes

Determine compliance by comparing direct-read exposure concentrations with respective enforcement exposure limits. Detector tube samples or electronic direct-reading instrument measurements should be taken in conjunction with diffusion tube samples to corroborate the full-shift data.

Example - the ceiling limit for nitrogen dioxide is 5 ppm. A detector tube grab sample taken in a miner's breathing zone read 10 ppm.

The error factor for Dräger NO_2 2/c detector tube # 6719101 is 1.25.
The enforcement ceiling limit = 1.25 x 5 ppm = 6.25 ppm.
The sample indicates a citable overexposure has occurred.

Example - the short-term exposure limit (STEL) for carbon monoxide (CO) is 400 ppm for a 15-minute exposure. Take partial-period sampling to determine compliance:

- •   Detector tube reading during the first 5-minute period was 250 ppm.
- •   Detector tube reading during the second 5-minute period was

> 600 ppm.
> - Detector tube reading during the final 5-minute period was 150 ppm.
> - Add the three readings and average (divide by 3) to obtain the concentration of the short-term exposure:

$$\text{Exposure Concentration} = \frac{250 \text{ ppm} + 600 \text{ ppm} + 150 \text{ ppm}}{3} = 333 \text{ ppm}$$

> The error factor for Dräger CO 5/c detector tube # CH25601 is 1.25.
> The enforcement STEL = 1.25 x 400 ppm = 500 ppm.
> The sample indicates compliance.

C.   Additive Effects

See Chapter 2 for a discussion of additive effects and calculation examples.

X.   Report Writing

A.   Inspection reports should include a copy of the Health Field Notes; the Area Sample Data Summary (ASDS) or Personal Exposure Data Summary (PEDS); appropriate citation/orders; and any other supplemental information collected during the inspection.

B.   Complete the Area Sample Data Summary (refer to Chapter 21, Section IX) or the Personal Exposure Data Summary (refer to Chapter 21, Section VIII), as applicable. List full-shift exposure samples as a single sample result. Do not list individual samples used as part of the full-shift exposure calculation. Any short-term or individual sampling results which exceed the short-term exposure limit (or the excursion or ceiling limit) or are not used in calculating a full-shift exposure may be listed separately. Be sure that the concentration and exposure limit units of measurement are the same as those listed for the contaminant code (refer to Chapter 3).