

VI. WORK PRACTICES

Work practices for handling carbon dioxide are limited to the handling of dry ice, entry into confined spaces, and cylinder handling. Generally, engineering controls as described in Chapter IV should be used to control exposure to the gaseous phase of carbon dioxide. The liquid will present no problem since it exists only under high pressure and therefore is confined to completely enclosed systems.

Prolonged skin contact with dry ice can result in frostbite. Therefore, suitable protective clothing, such as gloves and aprons which are resistant to temperatures lower than -109 F, should be worn.

Vaporizing dry ice and the presence of gaseous carbon dioxide in confined spaces can lead to excessive exposure to the gas. To avoid hazardous human exposures, confined spaces should be adequately ventilated and cleaned before employees are allowed to enter such areas. If entry is essential, suitable respiratory equipment shall be worn in accordance with the provisions of Table I-1. In addition, employees entering areas where respirator failure would result in overexposure to carbon dioxide shall be observed by at least one other person. Effective communication shall be maintained among all involved persons.

Cylinders of carbon dioxide should be handled in accordance with the recognized procedures described in 29 CFR 1910.166 and .168, and with the appropriate portions of 29 CFR 1910.252. The cylinders should be equipped with appropriate safety relief devices and pressure regulators.

Good engineering controls shall be employed to keep the concentration of gas within the prescribed environmental limits. The potential for

carbon dioxide to cause respiratory and CNS disorders and to cause unconsciousness at high concentrations requires that all reasonable safety precautions and work practices be employed to avoid the possibility of such human exposures.

VII. RESEARCH NEEDS

The preponderance of information on effects from the inhalation of increased carbon dioxide has been derived from studies of acute and chronic exposures. Although very few studies on the effects of intermittent exposures have been reported, the results suggest that the effects from intermittent exposures differ from those of both acute and chronic exposures. Justification for an occupational exposure limit should be based on intermittent exposures at low concentrations. Further, only one epidemiologic report has been found to date. There is a definite need to investigate these areas further.

The significance of carbon dioxide storage in bone and of its cardiac effects also needs to be considered. Other areas needing additional research are those relating to teratogenicity and possible reproductive problems attributable to carbon dioxide. The effects of exposure to carbon dioxide at concentrations below 1% (10,000 ppm) should be investigated.

Lack of relevant data has also limited the selection of sampling and analytical methods available for use in carbon dioxide monitoring. Scientific knowledge is available to design more efficient methods to determine the extent of worker exposure to carbon dioxide. The use of solid sorbents in personal sampling devices should be studied. In the past, the need for this information was not sufficient to merit exploration. This is definitely another area for immediate investigation to ensure effective compliance with the recommended standard.

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IX. APPENDIX I

SAMPLING METHOD FOR CARBON DIOXIDE

General Requirements

Samples representative of the air within the worker's breathing zone shall be collected. At the time of sample collection, the following shall be recorded:

- (a) Sampling location and conditions at the time of sample collection.
- (b) Time and date of sample collection.
- (c) Equipment used and rates of sampling.
- (d) Type of bag used for collection.
- (e) Any other information pertinent to the sample collection.

Air Sampling Equipment

(a) Diaphragm pump: a battery-operated pump capable of inflating plastic bags at a constant flowrate. The pump should have a clip or other suitable device to attach the pump to the worker's belt.

(b) Plastic bags: material with minimum bag loss and interference properties such as Tedlar, Mylar, Saranex. The bags must be properly cleaned and evacuated to minimize background interference.

X. APPENDIX II

ANALYTICAL METHOD FOR CARBON DIOXIDE

The analytical method is adapted from that described by Murray and Doe. [125] Any other method which is equivalent in accuracy, precision, and sensitivity to that described may be used. Such other methods may involve more sophisticated gas chromatographic techniques including Carbosieve-B columns or the use of infrared or nondispersive infrared spectrophotometers.

Principle of the Method

The analysis is based on the chromatographic separation of carbon dioxide from oxygen and nitrogen on a precut column of silica gel after the removal of water vapor by passage of the sample through Drierite. The sample is then passed through a second silica gel column (analytical column) and is quantified by a hot-wire thermal conductivity detector. A compensation column is included in the setup for a reference chromatogram. The compensation column is used to eliminate variations in detector response as a result of factors other than those inherent in the analytical sample.

Range and Sensitivity

The reported range of detection of the recommended analytical method is from 13 to 500 ppm with a minimum detection level of 13 ppm for a 95-ml

gas sample. For a 26-ml gas sample, the detectable range is from 20 to 500 ppm. The method may be used to detect concentrations of carbon dioxide at the recommended TWA environmental and ceiling limits by taking proportionately smaller aliquots (1.3 ml for 10,000 ppm, 3.9 ml for 30,000 ppm) of the air sampled.

Interferences

The column type specified had no reported interferences.

Precision and Accuracy

On 26-ml samples, the standard deviation for eight samples in both the average peak height and average peak area was $\pm 2\%$. On 95-ml samples, the standard deviation for nine samples in average peak height was $\pm 2\%$, while the deviation in average peak area was $\pm 5\%$.

Apparatus

- (a) Dual-column gas chromatograph equipped with a hot-wire thermal conductivity detector.
- (b) A mechanical or electronic integrator or a recorder and some method for determining peak area.
- (c) A gas-sampling valve with a sample loop or loops of known volume.
- (d) A four-way gas chromatograph selector valve located between the precut column and the analytical column.
- (e) A sample drying apparatus (Drierite). The sample is dried

before introduction into the gas chromatograph.

(f) A precut column made of 1/4-inch OD copper tubing, 3.5 feet, with 30-60 mesh silica gel. The precut column is located between the gas-sampling valve and the four-way selector valve. This column separates nitrogen and oxygen from the carbon dioxide so that these gases can be vented to the atmosphere before passing through the analytical column.

(g) Analytical and compensation columns of 1/4-inch OD copper tubing, 2.5 feet, with 30-60 mesh silica gel.

Reagents

- (a) Carbon dioxide, at known concentrations for controls.
- (b) Helium, equivalent to Bureau of Mines Grade A.

Analysis of Samples

(a) Preparation: Withdraw air from the bag into a gas-tight syringe and return to the bag several times to ensure that the air contained by the valve stem is the same as in the bag. Withdraw a measured volume of air for analysis by gas chromatography.

(b) Typical gas chromatographic operating conditions:

(1) Set the four-way valve so that the nitrogen and oxygen are vented to the atmosphere as the analytical column is purged with the helium carrier gas. The "vent time" depends on the carrier gas flowrate and is determined by the retention times of air and carbon dioxide in the precut column. Determine the retention times of air and carbon dioxide in the precut column indirectly by measuring the difference between their

retention times in the analytical column alone and in the entire precut and analytical column system. Using these calculated retention times for the precut column, choose a vent time intermediate between the retention time for the precut column and that for carbon dioxide.

(2) Maintain the precut column temperature at 60 C with asbestos insulation and electrical heating tape and the analytical and compensation columns at 40 C. Maintain the detector and injector temperatures higher than those of the columns, though not so high that condensation can occur.

(3) Set the helium gas flowrate either at 50 ml/minute in the analytical column and 70 ml/minute in the compensation column or according to individual instrument specifications.

(c) Dry the air samples by passage over Drierite and inject them through loops of appropriate volume.

(d) Measurement of area: Measure the areas of the sample peaks with an electronic integrator or some other suitable method of area measurement and read preliminary sample results from a standard curve.

(e) Calculation: Read the weight of carbon dioxide in mg, corresponding to the total peak area, from a standard curve. Express the concentration of carbon dioxide in the air sampled in mg/cu m (which is numerically equal to $\mu\text{g/liter}$ of air). This is given by the quotient of the amount of carbon dioxide in the sample, in μg , divided by the volume of the sample injected, in liters:

$$\text{concentration } (\mu\text{g/liter}) = \frac{\text{amount } (\mu\text{g})}{\text{volume (liters)}}$$

Another method of expressing concentration is ppm:

$$\text{concentration (ppm)} = \text{concentration } (\mu\text{g}) \times \frac{24.45}{44} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

24.45 = molar volume (liter/mole) at 25 C and 760 torr

44 = molecular weight of carbon dioxide

760 = standard pressure

P = pressure (torr) of air sampled

T = temperature (degrees C) of air sampled

298 = standard temperature (degrees K)

or

$$\text{concentration (ppm)} = \text{concentration } (\mu\text{g}) \times \frac{1.416 (T + 273)}{P}$$