VI. WORK PRACTICES

In the production and use of chromium(VI) materials, work practices must be designed to minimize or to prevent the inhalation of such materials and their contact with skin and eyes. Good work practices are a primary means of controlling certain exposures and will often supplement other control measures.

Enclosure of materials, processes, and operations is completely effective as a control only when the integrity of the system is maintained. Such systems should be inspected frequently for leaks and any leaks found should be promptly repaired. Special attention should be given to the condition of seals and joints, access ports, and other such places. [123] Similarly, points of wear or damage should be inspected regularly.

Ventilation systems require regular inspection and maintenance to ensure their effective operation. The effects of any changes or additions to the ventilating system or to the operations being ventilated should be assessed promptly, including measurements of air flow and of environmental levels of contaminants under the new conditions. Work practices should introduce no obstructions or interferences which would reduce the effectiveness of the ventilating system.

Because chromium(VI) compounds cause irritation of the skin, skin ulcers, and skin sensitization, contact with these materials should be prevented by full-body protective clothing consisting of (a) protection for the head, neck, and face, eg, a hat preferably with a broad brim, such as a full-brimmed hard hat or respirator hood, (b) coveralls or the equivalent, (c) impermeable gloves with gauntlets, and (d) shoes and apron where

solutions or dry materials containing chromium(VI) may be contacted.

The proper use of protective clothing requires that all openings be closed and that garments fit snugly about the neck, wrist, and ankles whenever the wearer is in an exposure area. Clean work clothing should be put on before each shift. At the end of the shift, the employee should remove the soiled clothing, place it in the covered container provided, and shower before proceeding to his locker to put on his street clothes. The shower should include a good lathering with soap. Care should be exercised to keep contaminated work clothing away from street clothing.

These procedures also apply when, during a shift, the work clothing becomes wetted or grossly contaminated with a material containing chromium(VI).

Gloves, aprons, goggles, face shields, and other personal protective devices must be maintained in good hygienic and uncontaminated condition. They should be cleaned or replaced frequently and on a regular schedule. Employees should keep such equipment in suitable, designated containers or places when the equipment is not in use.

Workers may reduce the potential exposures significantly by retiring to clean areas when their presence at the operation point is not necessary. A clean area may simply be a room or a space where sustained environmental levels are such that it can be considered as being without occupational exposure to chromium(VI). A clean area can be deliberately established by means of ventilation which provides either filtered air or air from an uncontaminated source in a manner and amount which maintains the environmental level of chromium(VI) at a nonexposure level.

In areas and at operation sites where the use of respiratory protection is required, the employee shall wear the designated type of respirator and observe the practices of the respiratory protective devices program. The necessity of cleanliness and maintenance of respirators should be emphasized. Practices which lead to the contamination of the interior of the facepiece should be prohibited.

When spills of chromium(VI) occur, they should be cleaned up promptly by means which will minimize any inhalation of, or contact with, the materials. Wet vacuuming is preferred for spills of dry material. Liquid or wet material spills should be flushed with an abundance of water. This liquid waste should be channeled to a treatment system or to a holding container for recycling or for safe disposal. Dikes should be sufficient to contain the volume of liquid from process or storage containers.

If chromium(VI) comes into contact with the skin, the affected area must be flushed promptly with large amounts of running water. When there is gross contact, the area should be washed with mild soap and water. The eyes, if splashed, sprayed, or otherwise contaminated with chromium(VI), must be flushed immediately for 15 minutes with a copious flow of water, then promptly be examined by a physician to determine the need for further treatment. The employee shall be fully informed of the need for carefully observing these procedures.

The duties of maintenance and repair workers pose special problems of potential contact and exposure. Often the very circumstances that require the maintenance or repair work and under which work must be done will negate some of the normal control procedures. Because of these factors, very careful supervisory control must be exercised for such activities.

The availability of an unrestricted supply of water near all workplaces where contact with chromium(VI) is likely is necessary. The water may be provided by a free-running hose, at low pressure, or by emergency showers. Where contact with the eyes is likely, eye-flushing fountains should be provided.

Careful attention to personal hygiene practices is important to the control of skin exposures.

Employees shall be fully informed of the hazards and of the proper work procedures. They should be trained to report promptly to their supervisor any leaks observed, failures of equipment or procedures, wet or dry spills, cases of gross contact, and instances of suspected overexposure. The employees should be instructed in the location and use of protective equipment and they should be periodically refreshed on these matters.

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VIII. APPENDIX I

SAMPLING AND CALIBRATION PROCEDURES

Sampling for Chromium(VI) [66]

Breathing zone air is drawn at the rate of 1-2 liters/minute through a 37-mm PVC filter having a 5-μm or smaller pore size mounted in a 2- or 3-piece cassette which is attached to the worker's collar. PVC is recommended because other materials may chemically reduce chromium(VI) to chromium(III). A portable battery-operated personal sampling pump connected to the cassette by flexible vinyl tubing and worn by the worker shall be used for sampling and must be calibrated (v.i.) in accordance with this appendix. Minimum sample volume for determining time-weighted average exposure to noncarcinogenic chromium(VI) should be 192 liters. For determining ceiling concentrations, the minimum sample volume should be 96 liters. Alternative sampling systems may be used, providing the necessary volume of air is sampled through a chemically inert filter in the breathing zone of the worker. The minimum quantity of chromium(VI) which must be collected in order to determine with reliability the presence or absence of chromium(VI) in a sample is 0.5 μg Cr(VI). In order to determine that chromium(VI) is present only in the workplace at concentrations less than 0.5 μg/cu m, it is necessary that each sample of airborne chromium(VI) that is analyzed for the purpose of making this determination be the residue from the filtration of at least 1.0 cu m of workplace air.

Upon completion of sampling, plastic caps should be replaced on the inlet and outlet openings of the cassette and an appropriate identifying number attached to it. Samples should be stable for periods up to 2 weeks, but should be analyzed as soon as possible.

Calibration

The accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured; the accurate calibration of a sampling device is essential to the correct interpretation of the volume indicator. The frequency of calibration depends on the use, care, and handling of the pump. Pumps should be calibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, it should be calibrated more frequently.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and at frequent intervals while being used. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument may depend largely upon where the calibration is to be performed. For laboratory testing, a soap-bubble flow meter (eg, an inverted buret), where appropriate, or wet-test meter is recommended, although other standard calibrating instruments such as a spirometer or dry-gas meter can be used. The actual set-up should be connected as shown in Figure XI-1. In this way, the calibration instrument will be at atmospheric pressure. Each personal sampling pump must be calibrated separately. If the inverted buret is used, it should be set up so that the flow is toward the narrow end of the unit.

Care must be exercised in the assembly procedure to ensure that seals at the joints are airtight; the length of connecting tubing in the calibration system upstream from the filter cassette should be minimized. The pump's rotameter must be calibrated with a representative filter and filterholder in the line. The temperature and pressure at which the pump's rotameter is calibrated should be recorded.

IX. APPENDIX II

ANALYTICAL CHEMICAL PROCEDURES FOR DETERMINATION OF CHROMIUM(VI)

Chromium(VI): The s-diphenylcarbazide method using a PVC filter and modifications made by Abell and Carlberg [66] is recommended.

Principle

Chromium(VI) airborne particulates are collected on a polyvinyl chloride (PVC) filter.

The filter is washed with dilute sulfuric acid, and s-diphenylcarbazide is added to form a colored complex.

The absorbance of the solution at 540 nm is determined and compared to the absorbance of standards.

Range and Sensitivity

When using 22-mm cells and a 15-ml final volume, an absorbance of 0.0044 occurs, which corresponds to a 1% reduction in % transmittance (%T), with about 0.05 μg of chromium(VI).

The useful range for the colorimetric method is 0.5-10 μg chromium(VI). For a 1000-liter air sample, this corresponds to 0.5-10 μg Cr(VI)/cu m. Dilutions are easily made.

Interferences

Possible interferences for the diphenylcarbazide method include many of the heavy metals. The elements likely to be encountered at appreciable levels are iron, copper, nickel, and vanadium. Tests show that 10 μg of

any of these causes an absorbance of less than 0.002 (a reduction of less than 0.5% transmittance), which is equivalent to about 0.02 μg chromium(VI).

Precision and Accuracy

Ten filters spiked with 1.0 μg of chromium(VI) (a 0.01-ml droplet of 100 ppm chromium(VI) standard solution was placed on each filter and allowed to dry) gave recoveries of 93% with a relative standard deviation of 3.2% when analyzed within 1 hour of deposition; after 1 week, the average recovery dropped to 50%. Twenty-two filters, each loaded with about 5 μg of chromium(VI) in a chromic acid mist generator, gave results with a relative standard deviation of 4.3%. No corroborative tests have been performed on this method.

Apparatus

22-mm round, matched cuvettes.

Filtering apparatus.

Spectrophotometer set to operate at 540 nm.

Reagents

Water: Unless otherwise designated, all water used is double distilled or deionized.

Half-normal sulfuric acid solution: Add 13.9 ml of concentrated sulfuric acid to some water in a 1-liter volumetric flask and dilute to mark. The exact concentration is not critical but it is suggested that the same solution be used for a complete test--samples, blanks, and standards.

After thorough mixing, it is convenient to transfer part of the solution to a small plastic wash bottle.

Diphenylcarbazide solution: Dissolve 0.50 g of s-diphenylcarbazide in a mixture of 100 ml of acetone and 100 ml of water. Store in a dark bottle in the refrigerator. The solution will remain stable for about 1 month.

Chromium(VI) standard solution: Dissolve 0.2829 g of potassium dichromate (reagent grade or better) in water in a 1-liter volumetric flask and dilute to mark. This solution is 100 ppm in chromium(VI).

Procedure

(a) Cleaning of equipment

(1) Wash all containers in hot, soapy, tap water and follow with tap and distilled water rinses.

(2) Soak in concentrated nitric acid (10% nitric acid for plastics) for 30 minutes. Rinse thoroughly with water.

(b) Collection and shipping of samples

(1) Samples are collected on PVC filters with 5-μm pore size. The temperature and pressure or elevation at which the samples are collected should be recorded.

(2) Air is drawn through the filter by means of an appropriate sampling pump. Some minimum sampling volumes for collection of approximately 0.5 μg chromium(VI) are:

Concentration to be measured, μg chromium(VI)/cu m	Minimum required sample size (liters)
0.5	1000
1.0	500
5.0	100
10.0	50
25.0	20

(3) With each batch of samples, 1 filter labeled as a blank should be submitted. This filter should be subjected to exactly the same handling as the samples except that no air is drawn through it.

(4) The samples should be shipped in a suitable container, designed to prevent damage in transit.

(c) Analysis of samples

(1) Pipet 15 ml of water into each cuvette to be used. Put a piece of tape on the cuvette so that its bottom edge matches the meniscus. Rinse the cuvettes.

(2) Blank filters are folded and placed directly into cuvettes. Sample filters are folded and placed in large test tubes.

(3) Six or 7 ml of 0.5 N sulfuric acid is added to each tube and the tube is shaken to assure that all surfaces of the filter are washed. The filters are removed from the tubes with small forceps with careful washing of all surfaces with an additional 1 or 2 ml of 0.5 N sulfuric acid. The washed filters are discarded.

(4) Solutions from actual samples should be filtered through a PVC filter when transferring them from the original tubes to 22-

mm cuvettes. This removes suspended particles. A No. 5, 2-hole stopper, if altered by enlarging 1 hole, can accommodate a small Buechner funnel and vacuum line and will fit a 22-mm cuvette. After the solution has filtered through, wash the funnel and filter with several milliliters of the 0.5 N sulfuric acid. Standards should be set up along with each set of samples being analyzed as in the section below on calibration and standards.

(5) Add 0.5 ml of the diphenylcarbazide solution to each cuvette. Then add more 0.5 N sulfuric acid until the meniscus matches the bottom edge of the tape. Shake the cuvette to mix, and wipe the outside with absorbent tissue.

Put 6-7 ml of 0.5 N sulfuric acid into each of 7 of the 22-mm cuvettes. Pipet 0,2, 5, 10, 20, 50, and 100 μl of the 100-ppm standard into the cuvettes forming 0-,0.2-,0.5-,1.0-,2.0-,5.0-, and 10.0-μg standards, respectively. Add 0.5 ml of the diphenylcarbazide solution and sufficient 0.5 N sulfuric acid to dilute to the 15-ml mark. Shake and wipe clean. The 0-μg standard is used to set the 0 absorbance reading of the spectrophotometer at 540 nm. The absorbances of the other standards are read and recorded along with those of the samples.

A calibration curve is drawn by plotting the absorbance of the standards against μg chromium(VI).

Calculations

Blank absorbance values, if any, should be subtracted from each sample absorbance value.

The indicated sampling rate must be corrected for deviations from the atmospheric temperature and pressure at which the pump's rotameter was calibrated. The correction equation is:

$$q(\text{actual}) = \frac{q\ (\text{indicated})\ \ P\ (\text{calibrated})}{P\ (\text{actual})} \times \frac{T\ (\text{actual})}{T\ (\text{calibrated})}$$

where: q = volumetric flow rate

P = atmospheric pressure

T = temperature (Kelvin or Rankine)

The concentration of chromium(VI) in air is calculated as follows:

$$\text{mg/cu m chromium(VI)} = \frac{\mu\text{g chromium(VI) from calibration curve}}{\text{liters of air sampled}}$$

Advantages and Disadvantages

The method is extremely simple, very selective for chromium(VI), and sensitive. The samples, when collected on PVC filters, are very stable. The recovery after 2 weeks is essentially the same as for the first day. Filters kept for 9 weeks gave an average recovery that was 79% of the first day's results. However, samples made by spiking PVC filters are not very stable and give poor recoveries. Spiked filters are therefore not recommended for standards.