

VII. APPENDIX I

AIR SAMPLING PRACTICES FOR CHROMIC ACID

General Requirements

Air concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include:

- (1) The date and time of sample collection
- (2) Sampling duration
- (3) Volumetric flowrate of sampling
- (4) A description of the sampling location
- (5) Other pertinent information

Breathing Zone Sampling

(a) Breathing zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and shall characterize the exposure from each job or specific operation in each production area.

(b) A portable battery-operated personal sampling pump plus an unweighed 0.8 μ cellulose membrane filter (Type AA) mounted in either a 2- or 3-piece cassette shall be used to collect the sample.

(c) The sampler shall be operated at a flowrate of two liters per minute and samples taken for at least 10 minutes.

(d) A minimum of three samples shall be taken for each operation (more samples if the concentrations are close to the standard) and averaged on a time-weighted basis.

(e) A minimum of three blank filters carried in closed cassettes to the sampling site shall be provided to the analytical laboratory to determine the background correction which must be applied to the analytical results.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the pump's indication. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been subjected to misuse or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a 1-liter burette or wet-test meter is recommended, although other standard calibrating instruments such as spirometer, Marriott's bottle, or dry-

gas meter can be used. The actual set-up will be the same for these instruments.

Instructions for calibration with the wet-test meter follow. If another calibration device is used, equivalent procedures should be followed.

(a) The calibration device used shall be in good working condition and shall have been calibrated against a spirometer (or other primary standard) upon procurement, after each repair, and at least annually.

(b) Calibration curves shall be established for each sampling pump and shall be used in adjusting the pumps prior to field use.

(c) The volumetric flowrate through the sampling system shall be spot checked and the proper adjustments made before and during each study to assure obtaining accurate airflow data.

(d) Flowmeter Calibration Test Method (see Figure 1)

(1) Apparatus

(A) Wet test meter (Arthur H. Thomas Co., Precision 5648-B10, or equivalent)

(B) Quick connector or by-pass valve

(C) In-line filter holder cassette with Type AA filter

(D) Tee

(E) Manometer (Dwyer No. 1215-36", U-tube or equivalent)

(F) Pump with rotameter (Mine Safety Appliances Co., Model G, or equivalent)

(G) Rubber or vinyl tubing

(H) Barometer

(I) Thermometer

(J) Stopwatch

(K) Small screw driver

(L) Graph paper

(2) Procedures

(A) Level wet test meter. Check the water level which should just touch the calibration point at the left side of the meter. If water level is low, add water 1 to 2 F warmer than room temperature to fill point. Run the meter for 30 minutes before calibration.

(B) Check the voltage of the pump battery with a voltmeter. For example, a reading of 7.0 volts for Mine Safety Appliances Company, Model G is required for calibration; and if reading is lower charge batteries until a reading of 7.0 volts is obtained.

(C) Mount the filter to be calibrated in the in-line filter holder.

(D) Assemble the calibration train as shown in Figure 1. Leave the quick connector disconnected.

(E) Turn the pump on, adjusting the rotameter with a screw driver to a reading of 10 (read middle of the float).

(F) Connect the wet test meter to the train. The pointer on the meter should run clockwise and a pressure drop of not more than 1.0 inch of water indicated. If the pressure drop is greater than 1.0 disconnect and check the system.

(G) Operate the system ten minutes before starting the calibration.

(H) Record the following on calibration data sheets:

(i) Wet test meter reading, start and finish

(ii) Elapsed time, start and finish

(iii) Pressure drop at manometer

(iv) Air temperature

(v) Barometric pressure

(vi) Serial number of pump and rotameter

(I) Adjust the rotameter reading to 9.0, 8.0, and 7.0, respectively, and repeat step (H) at each reading. Each point should run for 10 minutes or at least 0.5 cubic foot of air.

(J) Record the name of the person performing the calibration, the date, serial number of the wet test meter, and the numbers of the pump and flowmeter system being calibrated.

(K) Correct the wet test meter readings to standard conditions of pressure and temperature by means of the gas law equation.

(L) Use graph paper to record the actual airflow as the ordinate and the rotameter readings as the abscissa.

VIII. APPENDIX II

ANALYTICAL METHODS FOR CHROMIC ACID

Principle of the Method

(a) A known volume of air is drawn through a Type AA membrane filter to collect the chromic acid aerosol.

(b) The filter is placed in an individual plastic Petri dish and returned to the laboratory where the sample is leached from the filter with distilled water.

(c) The solution is filtered, if necessary.

(d) The hexavalent chromium is separated from trivalent chromium by chelation of the former with ammonium pyrrolidine dithiocarbamate (APDC) and extraction of the complex with methyl isobutyl ketone. [55]

(e) The extracted hexavalent chromium is analyzed by atomic absorption spectrophotometry.

(f) After correcting for the filter and reagent blank, the chromic acid concentration is calculated as milligrams chromium trioxide per cubic meter of air.

Range and Sensitivity

(a) The limit of detection of the method is 0.2 μg of chromic acid per filter sample or 0.01 mg chromic acid per cu m in a 20-liter air sample.

(b) The upper limit of the method may be varied, according to the sample requirements, by appropriate selection of the size aliquot portion taken for analysis and/or by changing the attenuation setting

of the spectrophotometer. The upper limit of the extraction procedure is 2.5 micrograms of hexavalent chromium [55] which would correspond to 0.25 mg of chromium trioxide per cu m in a nonaliquotted 20-liter air sample.

Interferences [55]

The method is essentially free from interference. The optimum pH for the extraction of the Cr-APDC complex by MIBK is 3.1. At this pH, however, manganese is partially extracted. The Mn-APDC complex is unstable and decomposes to a fine suspension of manganese oxides which clog the atomizer-burner. If the extract is not clear after standing overnight, it must be centrifuged. By adjusting the pH of the sample to 2.4 prior to chelation and extraction, less manganese is extracted and there is only a slight loss in the efficiency of the extraction of chromium.

Precision

(a) Single-operator precision of the method based on ten determinations of 5.0 μg of hexavalent chromium per liter in water solutions was reported to be 0.57 μg per liter. [55]

(b) No data are available currently on the accuracy of the overall analytical method.

Advantages and Disadvantages of the Method

(a) The method determines only hexavalent chromium in samples containing both trivalent and hexavalent forms of the element.

(b) The method is rapid and may be applied conveniently in all chemistry laboratories equipped with an atomic absorption spectrophotometer.

(c) The method is not affected by the presence of other common metallic elements with the exception of manganese; reduction of the pH of the sample solution from 3.1 to 2.4, prior to chelation and extraction of the hexavalent chromium, minimizes this effect.

Apparatus

(a) Filters, cellulose, membrane, 0.8 μ , Type AA

(b) Glassware, borosilicate, as required for the reagents Do not use polyethylene ware for chromium analyses

(c) Spectrophotometer, atomic absorption

Reagents

(a) Reagent grade chemicals shall be used in all tests.

(b) Water, demineralized (distilled or deionized), shall be used in preparing reagents or dilutions of samples.

(c) Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in demineralized water and dilute to 100 ml Prepare fresh daily.

(d) Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 ml 50% ethanol.

(e) Standard solution I. 1.00 ml = 100 μ g chromium: Dissolve 0.2829 g pure dried potassium dichromate in demineralized water and dilute to 1,000 ml.

(f) Standard solution II. 1.00 ml=10.0 μ g chromium: Dilute 100 ml chromium standard solution I to 1,000 ml with demineralized water.

(g) Standard solution III. 1.00 ml = 0.10 μ g chromium: Dilute 10.0 ml chromium standard solution II to 1,000 ml with demineralized water.

(h) Methyl isobutyl ketone (MIBK).

(i) Sodium hydroxide solution, 1M: Dissolve 40 g sodium hydroxide in demineralized water and dilute to 1 liter.

(j) Sulfuric acid, 0.12M: Slowly add 6.5 ml concentrated sulfuric acid (sp gr 1.84) to demineralized water and dilute to 1 liter.

(k) Wash acid - Add 50 ml of concentrated nitric acid to 150 ml of concentrated hydrochloric acid, mix and add to 200 ml of water. This solution may be used repeatedly to rinse glassware and should be stored in a borosilicate, glass-stoppered bottle.

Procedure

(a) Cleaning of glassware: Soak all glassware used for chromium analysis in detergent solution; rinse copiously with warm tap water; remove grease with alcoholic potassium hydroxide; rinse repeatedly with tap water to remove the residual caustic solution; rinse with the wash acid followed by repeated tap water and distilled water rinsings. Caution: Do not use chromic acid cleaning solution.

(b) Shipping of samples: Transfer each filter sample to an individual, covered, plastic Petri dish for transport to the laboratory.

(c) Analysis of Samples

(1) Transfer the filter containing the sample to a Griffin beaker and add sufficient demineralized water to cover the filter. Allow to stand for 10-15 minutes with occasional agitation.

(2) Decant the aqueous solution and demineralized water rinsings of the beaker into a 100-ml volumetric flask.

(3) Repeat steps (1) and (2) twice.

(4) Dilute the sample solution to volume and mix.

(5) Pipette a volume of the sample containing less than 2.5 μg of hexavalent chromium into a 200-ml volumetric flask and adjust the volume to approximately 100 ml.

(6) Prepare a set of 3 blanks, using filter papers carried through the leaching procedure described in Steps (1) through (5), and a set of hexavalent chromium standards; adjust the volume of each blank and each standard sample to approximately 100 ml.

(7) Add 2 drops of bromphenol blue indicator solution.

(8) Adjust the pH by addition of 1M sodium hydroxide solution by drops until a blue color persists. Add 0.12M sulfuric acid by drops until the blue color just disappears in both the standards and sample. Then add 2.0 ml 0.12M sulfuric acid in excess. The pH at this point should be 2.4.

(9) Add 5.0 ml APDC solution and mix. The pH should then be approximately 2.8.

(10) Add 10.0 ml MIBK and shake vigorously for 3 minutes.

(11) Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask. The Cr-APDC complex is stable for at least 36 hours.

(12) Aspirate the ketone layer and measure the absorbance (or other scale reading) of the solution against the average blank using the 3578.7 Å resonance line of chromium and the operating parameters of the atomic absorption spectrophotometer recommended by the manufacturer of the instrument for this determination. Repeat and average the duplicate results.

Calculations

(a) Prepare a plot of absorbance values (or other scale readings) of the series of standard samples whose concentrations are expressed as μg chromium trioxide per 10.0 ml of MIBK.

(b) Determine the μg chromium trioxide in the sample aliquot portion taken for analysis, using the standard curve prepared as described in Step (a).

(c) Calculate the μg chromium trioxide in the total filter sample and convert to milligrams.

(d) Divide the value obtained in Step (c) by the liters of air sampled and then multiply by 1000 to calculate the chromic acid

concentration in terms of milligrams chromium trioxide per cubic meter.

IX. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material containing chromic acid shall be provided in the appropriate section of the Material Safety Data Sheet or approved form. If a specific item of information is inapplicable (ie, flash point) initials "n.a." for not applicable shall be inserted.

(a) The product designation in the upper left hand corner of both front and back to facilitate filing and retrieval. Print in upper case letters in as large a print as possible.

(b) Section I. Source and Nomenclature.

(i) The name, address, and telephone number of the manufacturer or supplier of the product.

(ii) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(c) Section II. Hazardous Ingredients

(i) Chemical or widely recognized common name of all hazardous ingredients.

(ii) 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, 10-20% V; 10% max. W.

(iii) Basis for toxicity for each hazardous material such as established OSHA standard, in appropriate units and/or LD50, showing amount and mode of exposure and species, or LC50 showing concentration, duration of exposure, and species.

(d) Section III. Physical Data.

Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure, in millimeters of mercury, vapor density of gas or vapor (air=1), solubility in water, in parts per hundred parts of water by weight; specific gravity (water=1); percent volatile, indicate if by weight or volume, at 70 degrees Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether=1); and appearance and odor.

(e) Section IV. Fire and Explosion Hazard Data.

Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits, in percent by volume in air; suitable extinguishing media or agents; special fire fighting procedures; and unusual fire and explosion hazard information.

(f) Section V. Health Hazard Data.

Toxic level for total compound or mixture, relevant symptoms of exposure, skin and eye irritation properties, principal routes of absorption, effects of chronic (long-term) exposure, and emergency and first aid procedures.

(g) Section VI. Reactivity Data.

Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(h) Section VII. Spill or Leak Procedures.

Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers containing residues, contaminated absorbants, etc.

(i) Section VIII. Special Protection Information.

Requirements for personal protective equipment, such as respirators, eye protection, and protective clothing, and ventilation such as local exhaust (at site of product use or application), general, or other special types.

(j) Section IX. Special Precautions.

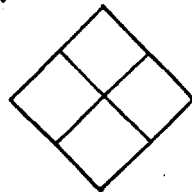
Any other general precautionary information such as personal protective equipment for exposure to the thermal decomposition products listed in Section VI, and to particulates formed by abrading a dry coating, such as by a power sanding disc.

(k) The signature of the responsible person filling out the data sheet, his address, and the date on which it is filled out.

PRODUCT DESIGNATION

**MATERIAL SAFETY
DATA SHEET**

Form Approved
Budget Bureau No.
Approval Expires
Form No. OSHA



SECTION I SOURCE AND NOMENCLATURE	
MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, ZIP Code)	
TRADE NAME AND SYNONYMS	CHEMICAL FAMILY
CHEMICAL NAME AND SYNONYMS	FORMULA

SECTION II HAZARDOUS INGREDIENTS					
BASIC MATERIAL	APPROXIMATE OR MAXIMUM % WT. OR VOL.	ESTABLISHED OSHA STANDARD	LD 50		LC 50
			ORAL	PERCUT.	SPECIES

SECTION III PHYSICAL DATA			
BOILING POINT	°F.	VAPOR PRESSURE	mm Hg.
MELTING POINT	°F.	VAPOR DENSITY (Air=1)	
SPECIFIC GRAVITY (H ₂ O=1)		EVAPORATION RATE (_____ =1)	
SOLUBILITY IN WATER	Pts/100 pts H ₂ O	VOLATILE	% Vol. % Wt.
APPEARANCE AND ODOR			

SECTION IV FIRE AND EXPLOSION HAZARD DATA		
FLASH POINT	FLAMMABLE (EXPLOSIVE) LIMITS	UPPER
METHOD USED		LOWER
EXTINGUISHING MEDIA		
SPECIAL FIRE FIGHTING PROCEDURES		
UNUSUAL FIRE AND EXPLOSION HAZARDS		

PRODUCT DESIGNATION

SECTION V HEALTH HAZARD DATA

TOXIC LEVEL

CARCINOGENIC

PRINCIPAL ROUTES OF ABSORPTION

SKIN AND EYE IRRITATION

RELEVANT SYMPTOMS OF EXPOSURE

EFFECTS OF CHRONIC EXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

SECTION VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

INCOMPATIBILITY (Materials to Avoid)

HAZARDOUS DECOMPOSITION PRODUCTS

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

WASTE DISPOSAL METHOD

SECTION VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS LOCAL EXHAUST

PROTECTIVE EQUIPMENT (Specify Types) EYE

MECHANICAL (General)

GLOVES

SPECIAL

RESPIRATOR

OTHER PROTECTIVE EQUIPMENT

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE

OTHER PRECAUTIONS

Signature _____

Address _____

Date _____

TABLE X-1

Physical Properties of Chromium Trioxide

Molecular Formula	CrO ₃
Formula Weight	99.99
Boiling Point	Decomposes
Melting Point	196 C
Density	2.70
Solubility	67.45 g per 100 g of water at 100 C; soluble in alcohol, ether, sulfuric acid, nitric acid

From reference number [6]

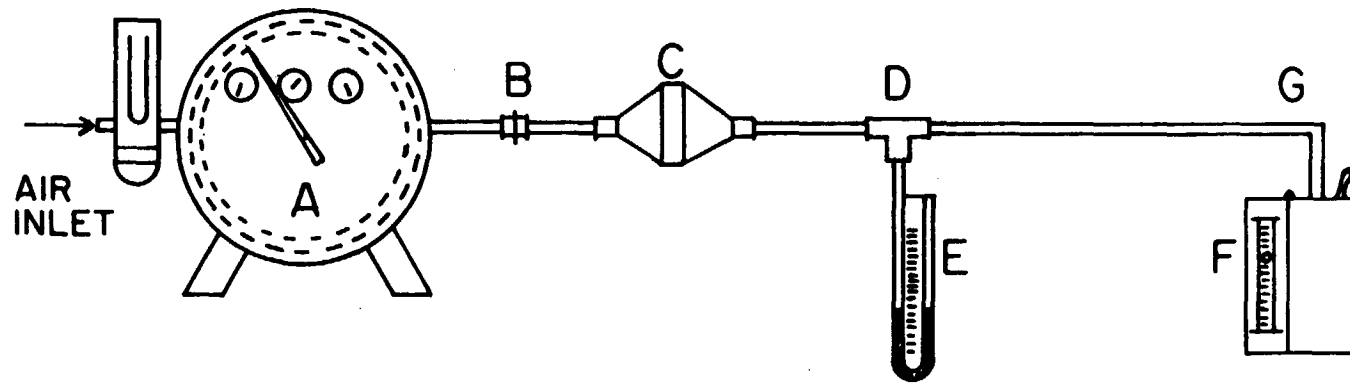


Figure 1. Calibration setup for portable pumps with filters .