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VIII. APPENDIX I

METHOD FOR SAMPLING CHLORINE IN AIR

General Requirements

In order to evaluate conformance with the environmental limit, chlorine concentrations in air shall be determined within the worker's breathing zone. Sampling procedures shall conform with the following criteria:

(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) Ambient temperature and pressure.

(6) Other pertinent information (eg, worker's name, shift, work process).

Breathing Zone Sampling

(a) Breathing zone samples shall be taken as near as practicable to the worker's face without interfering with his freedom of movement. Care should be taken that the bubbler is maintained in a vertical position during sampling.

(b) A portable, battery-operated, personal sampling pump capable of being calibrated to 5% at the required flow in conjunction with a midget fritted bubbler (coarse porosity) holding 10 ml of sampling solution shall be used to collect the sample.

(c) The sampling rate shall be accurately maintained at 1-2 liters/minute for a period of 15 minutes.

(d) A "blank" bubbler should be handled in the same manner as the bubblers containing the samples (ie, fill, seal, and transport) except that no air is sampled through this bubbler.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no better 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 volume indicator. 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 misused, 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 upon 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 buret (soapbubble flowmeter) or wet-test meter is

recommended, although other standard calibrating instruments, such as a spirometer, Marriott's bottle, or dry gas meter, can be used.

Instructions for calibration with the soapbubble flowmeter follow. However, if an alternative calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a midget bubbler is shown in Figure XIII-1.

(a) Check the voltage of the pump battery with a voltmeter both with the pump off and while it is operating to assure adequate voltage for calibration. If necessary, charge the battery to manufacturer's specifications.

(b) Fill the bubbler with 10 ml of the sampling solution.

(c) Assemble the sampling train as shown in Figure XIII-1.

(d) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and drawing bubbles up the inside of the buret until they are able to travel the entire length of the buret without bursting.

(e) Adjust the pump rotameter to provide a flowrate of 1.5 liters/minute.

(f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 13 inches of water (approximately 1 inch of mercury).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to travel a minimum of 1.0 liter.

(h) Repeat the procedure in (g) above at least three times, average the results, and calculate the flowrate by dividing the volume

between the preselected marks by the time required for the soapbubble to travel the distance.

(i) Data required for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

(j) Corrections to the flowrate may be necessary if the pressure or temperature when samples are collected differs significantly from that when calibration was performed. Flow rates may be calculated by using the following formula:

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

where: q = volumetric flowrate

P = pressure

T = temperature (Kelvin or Rankine)

(k) Use graph paper to record the air flow corrected to 25 C and 760 mmHg as the ordinate and the rotameter readings as the abscissa.

IX. APPENDIX II

METHOD FOR ANALYSIS OF AIR SAMPLES

Principle of Method [64]

Near a pH of 3.0, the color of a methyl orange solution nearly ceases to vary with increasing acidity. [64] At this pH, the dye may be quantitatively bleached by free chlorine and the extent of bleaching determined colorimetrically. The optimum concentration range is 0.05-1.0 ppm chlorine in ambient air (145-2900 μg/cu m at 25 C and 760 mmHg).

Apparatus

(a) Spectrophotometer suitable for measurement at 505 nm, preferably accommodating 5-cm cells.

(b) Midget fritted bubblers (coarse porosity) of 25-ml capacity.

(c) Sampling pump capable of a flowrate of 1-2 liters/min.

Reagents

Reagents must be ACS analytical reagent grade. Distilled water should conform to ASTM Standard for Reference Reagent Water, a blank standard.

(a) Methyl orange stock solution, 0.05%. Dissolve 0.500 g reagent grade methyl orange (sodium 4'-dimethylaminoazobenzene-4-sulfonate) in distilled water and dilute to 1 liter. This solution is stable indefinitely if freshly boiled and cooled distilled water is used.

(b) Methyl orange reagent, 0.005%. Dilute 100 ml of stock solution to 1.0 liter with distilled water. Prepare fresh for use.

(c) Sampling solution. Dilute 6 ml of 0.005% methyl orange reagent to 100 ml with distilled water. Add 3 drops (0.15-0.20 ml) of 5.0 N hydrochloric acid. One drop of butanol may be added to induce foaming and increase collection efficiency, although care must be taken to prevent the solution from foaming over during use. A practice test run is desirable.

(d) Acidified water. To 100 ml distilled water add 3 drops of 5 N hydrochloric acid.

(e) Potassium dichromate solution, 0.01000 N. Dissolve 0.4904 g anhydrous potassium dichromate, primary standard grade, in distilled water and dilute to 1.000 liter using a volumetric flask.

(f) Starch indicator solution. Prepare a thin paste of 1 g of soluble starch in a few milliliters of distilled water. Bring 200 ml of distilled water to a boil, remove from heat, and stir in the starch paste. Prepare fresh before each use.

(g) Potassium iodide, reagent grade.

(h) Sodium thiosulfate solution, 0.1 N. Dissolve 25 g of sodium thiosulfate pentahydrate in freshly boiled and cooled distilled water and dilute to 1.0 liter. Add 5 ml chloroform as preservative and allow to age for 2 weeks. If turbidity develops, discard the solution.

(i) Sodium thiosulfate solution, 0.01 N. Dilute 100 ml of the aged, 0.1 N sodium thiosulfate solution to 1.000 liter with freshly boiled and cooled distilled water using a volumetric flask. Add 5 ml chloroform

as preservative and store in a glass-stoppered bottle. Standardize before use with 0.01 N potassium dichromate as follows: to 80 ml distilled water add with constant stirring 1 ml concentrated sulfuric acid, 20 ml 0.01 N potassium dichromate, and approximately 0.1 g of potassium iodide. Allow to stand in the dark for 6 minutes. Titrate with 0.01 N thiosulfate solution. Upon approaching the end point (brown color changing to yellowish green) add 1 ml starch indicator solution and continue titrating to the end point (blue to light green). Repeat the standardization proce-

$$\text{Normality of sodium thiosulfate} = \frac{2.000}{\text{mls of sodium thiosulfate used}}$$

dure two more times. Calculate the average normality of sodium thiosulfate from the three titrations.

(j) Chlorine solution, approximately 100 ppm (100 μg/ml). Prepare by serial dilution of household bleach (approximately 50,000 ppm) or by dilution of strong chlorine water made by bubbling chlorine gas through cold distilled water. The diluted solution should contain approximately 100 ppm of free (available) chlorine. Prepare 1 liter.

Standards

(a) Prepare a series of six 10-ml volumetric flasks containing 0.6 ml 0.005% methyl orange reagent, 8.0 ml distilled water, and 20μl of 5.0 N HCl. Using Eppendorf pipets, carefully pipet 0, 5, 10, 25, 50, and 100μl chlorine solution (approximately 100 ppm) into the respective flasks, holding the pipet tip beneath the surface. Gently mix and dilute to volume with distilled water. The manner of addition of chlorine standards to

working solutions is important. The methyl orange solution is reported [69] to be less bleached by a rapid addition of halogen without stirring than by slow addition with vigorous mixing.

(b) Immediately standardize the 100-ppm chlorine solution as follows: to a flask containing 1 g potassium iodide and 5 ml glacial acetic acid add 50 ml chlorine solution, swirling to mix. Titrate with 0.01 N sodium thiosulfate until the iodine color becomes a faint yellow. Add 1 ml of starch indicator solution and continue the titration to the end point (blue to colorless). Standardize two additional 50-ml portions of the 100-ppm chlorine solution. Average these three values to obtain the exact titer of the approximately 100-ppm chlorine solution, then calculate the amounts of free chlorine added to each of the six volumetric flasks. One milliliter of 0.01 N sodium thiosulfate equals 354.6 μg of free chlorine. Compute the amounts of free chlorine added to each flask.

(c) Transfer the standards prepared as in (a) above to absorption cells and measure absorbance. Construct a standard curve by plotting absorbance versus micrograms of chlorine.

Sample treatment

(a) Place 10 ml of sampling solution in the fritted bubbler and draw a measured volume of air through the bubbler at a rate of 1-2 liters/min for 15 minutes. Transfer the solution to a 10-ml volumetric flask and dilute to volume, if necessary, with acidified water. Measure absorbance at 505 nm in 5-cm cells using distilled water as a reference.

(b) The volume of sampling solution, the concentration of methyl

orange in the sampling solution, the amount of air sampled, the size of the absorbing vessel, and the length of the photometer cell can be varied to suit the needs of the situation as long as proper attention is paid to the corresponding changes necessary in the standardization procedure.

Calculations

$$\text{ppm chlorine in air} = \frac{0.001 \times \mu\text{g chlorine found}}{\text{liters of air sampled}} \times 344.37$$

(at 25 C and 760 mmHg).

For different temperatures and atmospheric pressures proper correction for air volume must be made as follows:

$$\text{ppm chlorine in air} = \frac{0.001 \times \mu\text{g chlorine found}}{\text{liters of air sampled}} \times \frac{ABC}{D}$$

where: A = 22.4 μl chlorine/μmol chlorine at STP

$$B = \frac{\text{sampling temperature (K)}}{273\ \text{K}}$$

$$C = \frac{760\ \text{mmHg}}{\text{atmospheric pressure (mmHg)}}$$

D = 71 μg chlorine/μmol chlorine

Interferences

Free bromine, which gives the same reaction, interferes in a positive direction. Manganese(III) and manganese(IV) in concentrations of 0.1 ppm or above also interfere positively. In the gaseous state, interference from sulfur dioxide is minimal but, in solution, negative interference from sulfur dioxide is significant. Nitrites impart an off-color orange to the

methyl orange reagent. Nitrogen dioxide interferes positively, reacting as 20% chlorine. Sulfur dioxide interferes negatively, decreasing the chlorine by an amount equal to one-third the sulfur dioxide concentration. [64]

Sensitivity and Range

The procedure given is designed to cover the range of 5-100 μg of free chlorine/100 ml sampling solution. For a 30-liter air sample, this corresponds to approximately 0.05-1.0 ppm in air, the optimum range.

Precision and Accuracy

Chlorine concentrations have been measured by this procedure with an average error of less than ±5% of the amount present. [64]

Storage

The color of the sampled solutions is stable for 24 hours if protected from direct sunlight, although certain agents [iron(III)] may induce kinetic responses resulting in a slow color change.