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TGG: JCL: MMG: AJO: RF

XF: 253.1

VISTA

May 3, 1989

Mr. Vince Giovannatti
Millipore Corporation
7600 Penn Belt Drive
Forestville, MD ~~[illegible]~~ Southern ~~[illegible]~~ DPD Facility, MD 20747

Dear Vince:

In response to your questions regarding sampling for low levels of HCL in air, I am enclosing a summary and a detailed NIOSH sampling and analytical method.

I couldn't find any information on direct reading instrumentation in our files. However, I'll be at a conference this month with multiple exhibits on air sampling etc. and I'll look then. If I find anything good I'll let you know.

Sincerely,

Tom Grumbles dlj

Thomas G. Grumbles, C.I.H.
Environmental Quality Manager

dlj

Enclosures

3.2 Sulfide ion must be absent because it poisons the chloride ion electrode. Touch a drop of the sample to a piece of lead acetate paper to check for sulfide ion.

If sulfide is present, it is removed by addition of a small amount of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck a drop of the sample with lead acetate paper. Avoid a large excess of cadmium carbonate and long contact time with the solution. Filter the sample through a small plug of glass wool and proceed with the analysis.

3.3 Other common interfering ions are bromide ion, iodide ion, and cyanide ion. For interference-free operation, the chloride ion level must be at least 3×10^2 times the bromide ion level, 2×10^6 the iodide ion level, and 5×10^6 the cyanide ion level.

3.4 Sufficiently high concentrations of species which form extremely stable complexes with silver ion (such as ammonia and thiosulfate) will also interfere and will result in reading of higher chloride ion activity than actually exists. For less than a 1% error, the maximum ratio of ammonia to chloride concentration should be 0.12 and the maximum ratio of thiosulfate ion to chloride ion concentration should be 0.01.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.5-14 mg/cu m was 0.064. This value corresponds to a standard deviation of 0.45 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 A collection efficiency of 0.981 was determined for the collecting medium. On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.7% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 10.4.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur which would invalidate the sample. If more than 5% of the sample volume is lost, the sample should be discarded.

Hydrogen Chloride

Analyte:	Hydrogen Chloride	Method No.: S246
Matrix:	Air	Range: 3.5-14 mg/cu m
OSHA Standard:	5 ppm (7 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$): 0.064
Procedure:	Bubbler collection in 0.5 M sodium acetate, ion specific electrode	Validation Date: 1/30/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a midget bubbler containing 10 ml of sodium acetate solution.

   1.2 The resulting solution is diluted to 25 ml with distilled water.

   1.3 The diluted samples are analyzed using a chloride ion specific electrode.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3.5-14 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 15-liter sample. The probable useful range of this method is 1-20 mg/cu m for 15-liter samples.

   2.2 The upper limit of the range of the method is dependent on the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for hydrogen chloride was determined to be 0.981, standard deviation of 0.005 (essentially 1.00), when sampled for 15 minutes at 0.94 liter per minute from a test atmosphere containing 70 mg/cu m. Therefore, no correction for collection efficiency is necessary.

3. Interferences

   3.1 This method is not specific for hydrogen chloride since any chloride ion which is trapped in the bubbler will be measured and give a positive interference.

7.2 Collection Medium: 0.5 M sodium acetate solution. Dissolve 82 g of sodium acetate in doubly distilled water and dilute to 2 liters.

7.3 Sodium chloride, for preparation of standards.

7.4 Standard Chloride Solution.

7.4.1 Dissolve 0.384 g of sodium chloride in double distilled water and dilute to 1 liter for 10^{-2} M (Cl^-) or 354 µg Cl^-/ml. Adjust the pH to 5 with glacial acetic acid. This solution is stable for about two months. The following more dilute standards should be prepared fresh weekly and kept in polyethylene containers.

7.4.2 Dilute 10 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-3} M (Cl^-) or 35.4 µg Cl^-/ml.

7.4.3 Dilute 5 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 5×10^{-4} M (Cl^-) or 17.7 µg Cl^-/ml.

7.4.4 Dilute 3 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 3×10^{-4} M (Cl^-) or 10.6 µg Cl^-/ml.

7.4.5 Dilute 2 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 2×10^{-4} M (Cl^-) or 7.1 µg Cl^-/ml.

7.4.6 Dilute 1 ml 10^{-2} M (Cl^-) to 100 ml with 0.5 M sodium acetate for 10^{-4} M (Cl^-) or 3.5 µg Cl^-/ml.

8. Procedure

8.1 Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.

8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pour 10 ml of the collection medium (Section 7.2) into the midget bubbler, using a graduated cylinder to measure the volume.

8.3.2 Connect the bubbler (via the splashover tube) to the vacuum pump with a short piece of flexible tubing. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

6.1.1 A glass "midget bubbler" containing the collection medium (Section 7.2).

6.1.2 A pump suitable for delivering at least 1.0 liter per minute for 15 minutes. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Pipets: 1, 2, 3, 5, and 10 ml.

6.3 Orion Model 94-17A chloride specific ion electrode, or equivalent.

6.4 Reference electrode, Orion 90-02 double junction, or equivalent.

6.5 Expanded scale millivolt-pH meter, capable of measuring to within 0.5 millivolt.

6.6 Polyethylene beakers, 50-ml capacity. Premark the beakers by pipetting 25 ml of distilled water into each beaker and mark the liquid level. Pregraduated polyethylene beakers may be used. However, they should be checked as described above. Discard the water and dry the beakers.

6.7 Magnetic stirrer and stirring bars for 50-ml beakers.

6.8 Polyethylene containers. These containers should be used to store diluted sodium chloride standards and also for shipping of air samples.

6.9 100-ml volumetric flasks.

7. Reagents

All chemicals must be ACS reagent grade or equivalent.

7.1 Doubly distilled water.

8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, time and/or the volume as accurately as possible. Record the atmospheric pressure and the temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.4 The pump rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate and collection time.

8.3.6 After sampling remove the bubbler stem and transfer the contents of the bubbler to a polyethylene container. Rinse the bubbler and bubbler stem with 3-5 ml of collection medium, adding the rinse to the polyethylene container. Seal the polyethylene container with the associated caps just prior to shipment.

8.3.7 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.3.8 Whenever possible, hand delivery of the samples is recommended. Otherwise, special shipping cases designed by NIOSH should be used to ship the samples.

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

8.4 Analysis of Samples

8.4.1 The sample in each polyethylene container is analyzed separately.

8.4.2 Quantitatively transfer the contents of each polyethylene container to a 50-ml polyethylene beaker which has been pre-marked at 25 ml. Rinse the polyethylene container with 2-3 ml of distilled water and add rinse to the beaker. Adjust the pH to 5 with acetic acid and check the pH with pH paper. Dilute each sample to 25 ml with distilled water and stir the samples with a magnetic stirrer.

8.4.3 Lower the chloride ion specific electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mv) after it has stabilized (drift less than 0.5 mv/min).

9. Calibration and Standards

9.1 Prepare a series of chloride standard solutions in the pre-marked 50-ml beakers by diluting 10 ml of each of the chloride standards prepared in Section 7.4.2-7.4.6, to a volume of 25 ml with double distilled water, starting with the most dilute standard. Place the chloride ion electrode and the double reference electrode in the stirred solution. Record the resultant millivolt readings to the nearest 0.5 millivolt.

9.2 Plot the millivolt readings vs. the chloride ion concentrations of the standards on semi-log paper. The chloride ion concentration in μg/25 ml is plotted on the logarithmic axis.

10. Calculations

10.1 Read the weight in μg corresponding to each millivolt reading from the standard curve. No volume corrections are needed, because the standard curve is based on μg/25 ml volume, and the volume of the samples is identical to the volume of the standards.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample container
μg blank = μg found in blank container

10.3 Calculate the μg of hydrogen chloride by multiplying the μg chloride ion found (Section 10.2) by 1.028, which is the conversion factor to convert μg chloride ion to μg hydrogen chloride.

10.4 The concentration of the analyte in air sampled can be expressed in mg/cu m (mg/cu m = μg/liter).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.3)}}{\text{Air volume sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 "Analytical Method for Chloride in Air," Health Laboratory Science, Vol. 12, No. 3, (July 1975), 253-258.

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Sampling Data Sheet # S246

Substance:

Hydrogen Chloride

Standard:

8-hour time-weighted average: 5 ppm (7 mg/cu m) - Ceiling

Reference: 29 CFR 1910.93

Method:

A known volume of air is drawn through a midget bubbler containing 10 ml of 0.5 M sodium acetate to trap hydrogen chloride. The resulting solution is diluted to 25 ml with distilled water. The sample is analyzed using a chloride ion specific electrode and an expanded scale millivolt/pH meter. The method has been validated over the range of 3.5-14 mg/cu m for a 15-liter sample at an atmospheric temperature and pressure of 22°C and 764 mm Hg.

Sampling Equipment:

A calibrated personal sampling pump whose flow can be determined accurately, ± 5%, at 1.0 liter per minute, plus midget bubbler, containing 10 ml of 0.5 M sodium acetate. The sampling pump is protected from splashover by a 5-cm long by 6-mm I.D. glass splashover tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump. (An additional 100 ml of collection medium should accompany each set of bubblers for use in rinsing the bubbler and bubbler stems after sampling.) Samples are shipped in polyethylene containers.

Sample Size:

A sample size of 15 liters, taken at a flow of 1.0 liter per minute for 15 minutes, is recommended.

Sampling Procedure:

1. Connect the midget bubbler (containing 10 ml of the collection medium) with a 5-cm glass splashover tube containing the glass wool plug to the personal sampling pump using short pieces of flexible tubing.

2. The bubbler must be maintained in a vertical position during sampling.

3. Air being sampled should not be passed through any hose or tubing before entering the bubbler.

4. Set the flow rate as accurately as possible using the manufacturer's directions. Position the middle of the rotameter ball of the personal sampling pump to the 1.0 liter per minute calibration mark as accurately as possible. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation.

5. After sampling remove the bubbler stem and transfer the contents of the bubbler to a polyethylene container. Rinse the bubbler and bubbler stem with 3-5 ml of collection medium, adding the rinse to a polyethylene container. Seal the polyethylene container with the associated caps just prior to shipment.

6. Care should be taken to minimize spillage or loss by evaporation.

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

Special Considerations:

1. Where interfering compounds such as chlorides are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

2. Samples must be shipped in polyethylene containers instead of the bubbler bottoms. Samples stored in glass vials were found to be unstable after being stored for one week.

Shipping Instructions:

Whenever possible, hand delivery of the samples is recommended. Otherwise, special shipping cases designed by NIOSH should be used to ship the samples.

Reference:

Hydrogen Chloride, NIOSH Method No. S246.