Chlorine sampling techniques

The OSHA sampling and analytical method for chlorine is discussed in reference 9. 1. The principle of sampling is described in reference 9. 2. The analytical procedure is based on an iodometric technique which uses a residual chlorine electrode (RCE) for detection (9. 3.). The validation of the chlorine method consisted of the following experimental studies:

Analysis of a total of eighteen samples (six samples at each of the three test levels) which were prepared by adding known amounts of standardized chlorine solution to 0. 1% sulfamic acid collecting solution.

Analysis of a set of eighteen samples (six samples at each of the three test levels) collected from dynamically generated test atmospheres at approximately 0. 5, 1, and 2 times the OSHA Permissible Exposure Limit (PEL) of 1 ppm.

Determination of the collection efficiency of the 0. 1% sulfamic acid sampling solution.

Determination of potential breakthrough when sampling.

Determination of the storage stability over 30 days for collected samples.

Comparison with an independent method.

The details with respect to each of these items are discussed in the following sections. All experiments were based on the ability of the method to collect and analyze a 15-L air sample for each concentration tested. The sample preparation and analytical technique used during the method evaluation

follow that described in reference 9. 4. A revised method (9. 1.) is also available.

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Note: The revised version of the method (9. 1.) differs in one major point from reference 9. 4.: Preparation of samples and standards for analysis. It is now recommended to prepare samples and standards in 0. 1% sulfamic acid solutions rather than the deionized water previously used (9. 5.).

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A dynamic standard generator (Model 350, Analytical Instrument Development Inc., Avondale, PA) was used for generating test atmospheres of chlorine. The system is further described in reference 9. 6. Two chlorine permeation vials were used as the chlorine source. The permeation vials were maintained at a constant temperature of 30 0. 1 C. The chlorine concentration was determined from the weight loss of the permeation vial over a measured time period and was calculated according to the equation listed in Appendix A. After the chlorine was produced it was then diluted with tempered air so that a controlled concentration at 80% RH and 25 C was achieved. Flow rates for the generation system were measured with a soap bubble flow meter to accurately determine dilution and the final concentration of the gas.

Samples were taken from a glass sampling manifold which was attached to the generation system. The majority of samples were collected in sets of six at one of three concentrations, about 0. 5, 1, or 2 ppm chlorine.

Procedure: Samples containing 0. 1% sulfamic acid were spiked with standardized chlorine solutions. This test determined the precision and accuracy of the analysis portion of the method.

Results: The results are shown in Table 1. Average analytical recovery was 96. 7% and the coefficient of variation (CV1) was 0. 03 for the three sets of spiked samples.

Procedure: Samples were collected in 0. 1% sulfamic acid solutions at three different chlorine concentrations using the generation system described in Section 1. Midget fritted glass bubblers (MFGB) were used to disperse the air samples in the sulfamic acid solutions. This test determined the precision and accuracy of the sampling and analysis portion of the method.

Results: Sampling and analysis data are presented in Table 2. The NIOSH Statistical Protocol (9. 7.) developed for evaluation of methods under the Standards Completion Program (SCP) was used as a guide for the determination of precision and accuracy from this data. The precision for this method using these statistical procedures is:

The average recovery for sampling and analysis over all levels was 99. 4%. Any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. The Bartlett's test for homogeneity of variances and an outlier test (9. 7.) were applied to this data. The sampling and analysis data passed the Bartlett's test, indicating the CVs could be pooled for all sets of generated samples. One data point in the third set (2 PEL, n= 5) was rejected as an outlier.

Procedure: The collection efficiency (CE) of MFGBs containing 0. 1% sulfamic acid was assessed. A chlorine concentration of approximately 2 ppm was generated and samples were collected in series using the MFGBs. A flow rate of 1 L/min and a 15-min sampling period were used. The amount of chlorine collected in each of the two bubblers connected in series was measured.

Results: The results are shown in Table 3. The CE of the single bubbler was determined to be 1. 00; therefore, a recovery correction or sampling train is not necessary.

Procedure: Breakthrough is defined as the time the effluent concentration in a second bubbler (containing 0. 1% sulfamic acid) connected in series reaches 5% of the concentration of the test gas mixture. A test for breakthrough was conducted at about 2 ppm and at a 1 L/min sample collection flow rate. A sample set consisting of two bubblers in series was used to collect samples for each time interval listed: 15, 30, 60, 120, 180, and 240 min.

Results: No breakthrough occurred at this flow rate, during these sampling times, or at the concentration tested. The results are given in Table 4.

Procedure: A study was conducted to assess whether chlorine samples collected at the 1 ppm PEL could be successfully stored in the 0. 1% sulfamic acid collection solution. After sample collection using MFGBs, samples were transferred into 20-mL vials, capped with Teflon-lined caps, and stored at ambient laboratory temperatures in a dark environment for 1, 5, 15, or 30 days before analysis.

Results: Samples analyzed after 30 days were found to be within 3% of those analyzed immediately. Thus, storage does not represent a source of bias that would need to be corrected in the method. Storage stability data are presented in Table 5.

An independent volumetric method (9. 8.) involving a thiosulfate titration was used to determine the concentration of chlorine used for spiking. Chlorine gas was generated at a theoretical concentration which would give a chlorine concentration of 21. 70 g/mL in a specified volume of sulfamic acid. This value was calculated using the equation given in Appendix A. The gas was collected in 0. 1% sulfamic acid solution which was then used as a chlorine stock solution for spiked samples (Section 2.). All other samples were taken using the generation system. Analyses of the stock solution were performed using the RCE and the thiosulfate titration methods. The following results were obtained:

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The average value of 20. 69 g/ml from both methods was used as the stock solution concentration for the spiked samples mentioned in Section 2.

This sampling and analytical method has been shown to be precise and accurate at exposures near the OSHA PEL of 1 ppm when using 15-L air volumes. Breakthrough or storage stability do not pose significant problems under the conditions tested.

The development and evaluation of this method took place when the OSHA PEL for chlorine was a Ceiling value (15-min samples were taken). Although long-term samples were only taken during breakthrough studies, the data appears to indicate the method is capable of taking samples for chlorine TWA assessments. Two 4-h samples are recommended for TWA determinations of chlorine. When considering the amount of chlorine collected (as mass), any samples taken near the TWA PEL of 0. 5 ppm will have slightly larger mass concentrations of chlorine than those tested for this evaluation. In addition, during the evaluation no breakthrough was noted after 240 minutes of sampling and collection efficiency was excellent after 15 minutes of sampling. Both of these experiments were conducted at approximately 4 times the TWA PEL of 0. 5 ppm.

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