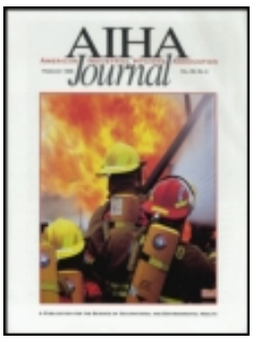

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Evaluation of Sampling and Analytical Methods for the Determination of Chlorodifluoromethane in Air

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In January 1989, the Occupational Safety and Health Administration (OSHA) published revised permissible exposure limits (PELs) for 212 compounds and established PELs for 164 additional compounds. In cases where regulated compounds did not have specific sampling and analytical methods, methods were suggested by OSHA. The National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM) Method 1020, which was developed for 1,1,2-trichloro-1,2,2-trifluoroethane, was suggested by OSHA for the determination of chlorodifluoromethane in workplace air. Because this method was developed for a liquid and chlorodifluoromethane is a gas, the ability of NMAM Method 1020 to adequately sample and quantitate chlorodifluoromethane was questioned and tested by researchers at NIOSH. The evaluation of NMAM Method 1020 for chlorodifluoromethane showed that the capacity of the 100/50-mg charcoal sorbent bed was limited, the standard preparation procedure was incorrect for a gas analyte, and the analyte had low solubility in carbon disulfide. NMAM Method 1018, for dichlorodifluoromethane uses two coconut-shell charcoal tubes in series, a 400/200-mg tube followed by a 100/50-mg tube, which are desorbed with methylene chloride. This method was evaluated for chlorodifluoromethane. Test atmospheres, with chlorodifluoromethane concentrations from 0.5–2 times the PEL were generated. Modifications of NMAM Method 1018 included changes in the standard preparation procedure, and the gas chromatograph was equipped with a capillary column. These revisions to NMAM 1018 resulted in a 96.5% recovery and a total precision for the method of 7.1% for chlorodifluoromethane. No significant bias in the method was found. Results indicate that the revised NMAM Method 1018 is suitable for the determination of chlorodifluoromethane in workplace air.

Chlorodifluoromethane is a chemically inert, nonflammable, nonexplosive gas at standard conditions, which liquifies when subjected to a pressure greater than atmospheric pressure. The possibility of occupational exposure to chlorodifluoromethane exists in industries that manufacture or use chlorofluorocarbons in the production of pesticides, air conditioners, and plastics, and in medical centers where it is used as a tissue-freezing agent. Studies of occupational hazards have found chlorodifluoromethane to be the possible cause of increased heart palpitations.[1] To limit worker inhalation exposure, a National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL),[2] an Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL),[3] and an American Conference of Governmental Industrial Hygienists Threshold Limit Value (TLV)[4] of 1000 ppm (3500 mg/m^3) have been established for full-shift time-weighted average (TWA) exposures to the vapors in air. Also, a NIOSH short-term exposure limit (STEL) has been set at 1250 ppm (4420 mg/m^3) for any 15-min exposure period.[2]

In January 1989, OSHA suggested that the NIOSH *Manual of Analytical Methods* (NMAM) Method 1020[5] be used to estimate the concentration of chlorodifluoromethane in workplace air.[3] This method, developed to determine 1,1,2-trichloro-1,2,2-trifluoro-ethane (a liquid at standard conditions), had not been evaluated for chlorodifluoromethane. The ability of NMAM Method 1020 to determine

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chlorodifluoromethane was of concern because of the difference in the physical states of the compounds at standard conditions, i.e., a liquid vs. a gas. NMAM Method 1018[6] for similiar gases, dichlorodifluoromethane and dichlorotetrafluoroethane, was thought to be a more appropriate choice for chlorodifluoromethane. Another NIOSH method, NMAM Method 2516[7] for dichloromonofluoromethane, was also a possibility. Because of the OSHA suggestion that NMAM Method 1020 be used for chlorodifluoromethane, the performance of NMAM Methods 1020, 2516, and 1018 for the quantification of chlorodifluoromethane was investigated.

All three methods involve collection of air samples on coconut-shell charcoal, solvent desorption of analyte, and quantitative analysis by gas chromatography with a packed column. The differences between the methods are in the size and number of charcoal tubes, and the desorption solvent. During the NIOSH/OSHA Standards Completion Program, it was determined that the sampling capacity of the 100/50-mg charcoal bed for the three gases was limited and that the two gases with more than one fluorine did not readily dissolve in carbon disulfide.[8-10] These problems were corrected with NIOSH Methods S108,[11] S109[12] and S111.[13] Methods S108 and S111 were later combined and revised as NMAM Method 1018. Method S109 was revised to be NMAM Method 2516. NMAM Method 1018 was chosen for chlorodifluoromethane when the problems of limited capacity of the small charcoal tube and reduced solubility in carbon disulfide were observed. None of the NMAM methods described an acceptable procedure for the preparation of gas standards, and therefore the approach provided in the NIOSH Method S111 for gas standards was used in this evaluation.

EXPERIMENTAL

Chemicals

Chlorodifluoromethane (99.9+%, from Aldrich Chemical Company, Milwaukee, WI) was contained in a low-pressure canister with a brass regulator and standard valve. The carbon disulfide, spectrophotometric grade, was acquired from EM Science, (Gibbstown, NJ), and methylene chloride, HPLC grade, came from Baxter Healthcare Corporation, Burdick and Jackson Division (Muskegan, MI).

Instrumentation

Analyses were performed on a Hewlett-Packard (Palo Alto, CA) model 5890 gas chromatograph equipped with a flame-ionization detector, a Hewlett-Packard model 7673A autosampler, and a Hewlett-Packard model 3392A integrator. The integrator was used to observe characteristic peaks and to operate autosampler functions, but the chromatographic data was collected on a Hewlett-Packard 3357 Laboratory Automation System. A 1-μL aliquot of the sample or standard was injected using splitless mode. A DB-1 fused silica capillary column, from J&W Scientific (Folsom, CA), 30 m long, with a 1.0-μm film thickness and a 0.32 mm i.d., was used for all analyses.

To obtain adequate separation of analyte from solvent, the gas chromatograph was temperature programmed. After an initial hold for 3 min at 35° C, the temperature was increased at a rate of 15°/min until reaching a final temperature of 75° C, with a final hold of 6 min. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. The solution was injected into the gas chromatograph in splitless mode with a purge time of 0.5 min and an injector temperature of 200° C. The flame ionization detector was set at 260° C.

Generation of Test Atmospheres

A wet-test meter (Precision Scientific Co., Chicago, IL), equipped with a wet-bulb thermometer, was used to measure air flow when generating test atmospheres of chlorodifluoromethane. The wet-bulb thermometer was used to calculate humidity of the collected air. Test atmospheres were prepared in 0.5- to 30-L aluminum-lined polyvinylchloride (PVC) collection bags (Calibrated Instruments Inc., Ardsley, NY), which were equipped with on/off valves. A known volume of air flowed into the gas bag while a measured amount of chlorodifluoromethane was injected into the stream via a polyethylene union tee, with a luer-lock syringe needle tightly fitted into one arm. The union tee fitted with a syringe needle was also used to introduce chlorodifluoromethane onto charcoal directly for recovery determinations. At least 0.5 L of air was allowed to pass after the addition of the analyte to the air stream. The gas-bag valve was closed and the bag was lightly kneaded to aid in the dispersal of the gas.

Sample Collection

Samples were collected from prepared bag atmospheres on coconut-shell charcoal tubes, Lot 120, obtained from SKC Inc. (Eighty Four, PA). For evaluation of NMAM Method 1020, one 150-mg charcoal tube, comprised of a 100-mg front section and a 50-mg back section, was used. NMAM 1018 required a 400/200-mg and a 100/50-mg charcoal tube connected in series. Sampling pumps (Dupont, Wilmington, DE, Model #P-30 and #P-125), calibrated at 25 and 40 cc/min, were used for drawing chlorodifluoromethane onto the charcoal and in preparing air concentrations for sample stability, and precision and accuracy experiments.

Preparation of Standards

A 20-mL calibrated automatic dispenser (Repipet™, Labindustries Inc., Berkeley, CA) was used to measure and dispense methylene chloride and carbon disulfide. Two 10-mL portions of solvent were dispensed into 20-mL screw cap vials containing silicone septa lined with polytetrafluoroethylene (PTFE) from Fisher Scientific (Pittsburgh, PA). Hamilton (Reno, NV) gas-tight syringes, 10-μL–10 mL, with luer-lock hubs and needles, were used to extract pure

chlorodifluoromethane from a canister. The chlorodifluoromethane in the syringe was then allowed to equilibrate to room temperature and pressure. An appropriate amount of gas was then forced out of the syringe, retaining the desired amount of analyte. The volume of chlorodifluoromethane was corrected to standard temperature and pressure using the Ideal Gas Law. This value, along with the fact that one mole of chlorodifluoromethane would occupy 24.45 L at standard conditions, was used to determine the actual milligram quantity of analyte added to each standard or sample. After the needle was inserted through the vial septum and immersed into the solvent, the gas was slowly released through the liquid and the bottle was shaken gently. Each day of sample analysis, 5–10 standards were prepared and analyzed concurrently. The concentration of the standards covered the range from one-half to twice the projected concentrations of the samples. A 2-mL Hamilton gas-tight syringe was used to transfer solutions to 1-mL crimp-cap autosampler vials.

Determination of Limit of Detection

To determine the limit of detection (LOD) of chlorodifluoromethane, low-level calibration standards were prepared as described in desorption efficiency experiments.[14] The expected LOD was 0.01 mg. Amounts of chlorodifluoromethane, not exceeding 0.1 mg (10× the expected LOD), were added to six charcoal tubes. These calibrated standards were then desorbed with 20 mL of methylene chloride and analyzed the same day.

Determination of Desorption Efficiency

The recovery of chlorodifluoromethane from coconut shell charcoal was determined by adding known quantities of analyte, 0.35–10.4 mg, to a flowing stream of air, 40 cc/min, which was drawn through the charcoal tube. Flexible plastic tubing, Tygon™, (6-mm i.d.) was used for all connections. After a known amount of analyte was drawn into a syringe, the syringe was fitted onto the needle in the union tee. The apparatus was arranged with the sorbent tube(s) orientated at a 45° angle from the horizontal to limit the possibility of channelling. The gas was slowly forced out of the syringe into the path of flowing laboratory air. Air was allowed to flow through the system for an additional 30–60 seconds after the release of the gas. Five sets of six tubes were fortified with chlorodifluoromethane, capped immediately, and stored at ambient temperature overnight. These samples were desorbed with 20 mL of methylene chloride and quantitatively analyzed to determine percent recovery upon desorption.

Capacity Determinations

The capacity of charcoal for chlorodifluoromethane was evaluated by determining the breakthrough volume of chlorodifluoromethane for each size sampling tube. Humid air concentrations (75–80% relative humidity) of chlorodifluoromethane at approximately 2x PEL were generated and drawn through a charcoal tube at 15–40 cc/min. A Halide Meter (GasTech Inc., Mountain View, CA), with the range set at 3, was connected to the outlet end of the sampling pump to detect breakthrough of analyte. The halide meter response, monitored by a strip chart recorder, was calibrated by drawing known concentrations (175–7000 mg/m^3) of chlorodifluoromethane through the meter without a charcoal tube in line. An average concentration of 6460 mg/m^3 was then drawn through a charcoal tube until the effluent gave a response that was equal to that obtained without a charcoal tube. The breakthrough volume was defined to be the sampling volume at which the effluent concentration from the tube was 5% of the air concentration being sampled.

A second technique was used for further evaluation of the capacity of the 400/200-mg charcoal tube. For this procedure, a known amount (3.5–10.6 mg) of chlorodifluoromethane was introduced into a stream of humid air being pulled at 15–40 cc/min through the charcoal tube. After the addition of the chlorodifluoro-methane was complete, a flow of clean humid air was continued until the effluent from the tube, monitored by the halide meter, gave a response greater than the response expected for 5% of the theoretical concentration based on sample volume and the amount of analyte added to the flowing air stream.

Precision and Accuracy Samples

Samples for the determination of the precision and accuracy of the method were collected one at a time with two 400/200-mg charcoal tubes connected in line. Once a test atmosphere was generated, the air was pulled through the tubes for 25–68 min at a rate of 40 cc/min. Chlorodifluoromethane air concentrations of 1779, 3515, and 6972 mg/m^3 were generated. A set of six samples (12 tubes) was collected at each concentration. The front and back tubes of each sample were capped immediately and stored separately at ambient conditions overnight.

Sample Stability Samples

Test atmospheres with average concentrations of chlorodifluoromethane of 3533 mg/m^3 were generated as described above. Samples were collected one at a time as in precision and accuracy experiments, but no back tube was used. A set of 48 samples was collected, stored at ambient temperature, and analyzed in groups of 3 over 36 days. A second set of 24 samples was collected and stored at 0° C and analyzed in groups of 3 over a 57-day period.

Sample Analysis

A 20-mL portion of methylene chloride was dispensed into a 20-mL screw cap vial. The urethane foam plug from the back end of the tube was removed, and the 200-mg portion of charcoal was transferred to the vial. Next, the urethane foam plug, which separated the two sections of the tube, was removed and the 400-mg section of charcoal was transferred to the same vial. A screw cap, equipped with a

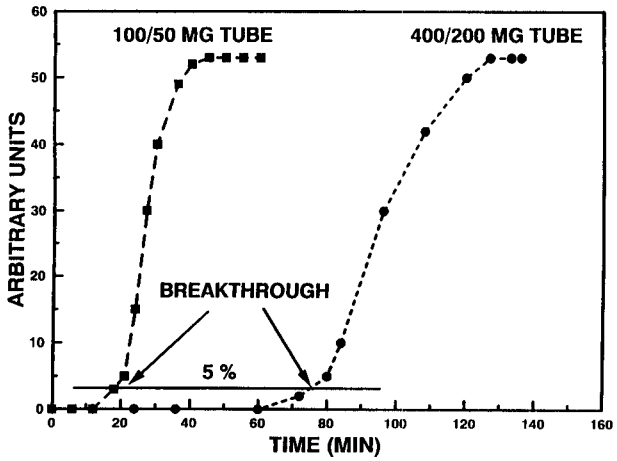

Figure 1. Conventional breakthrough curves of chlorodifluoromethane from 100/50- and 400/200-mg charcoal tubes. The concentration of the atmosphere sampled was 6990 mg/m³ and the sampling flow rate was 25 cc/min.

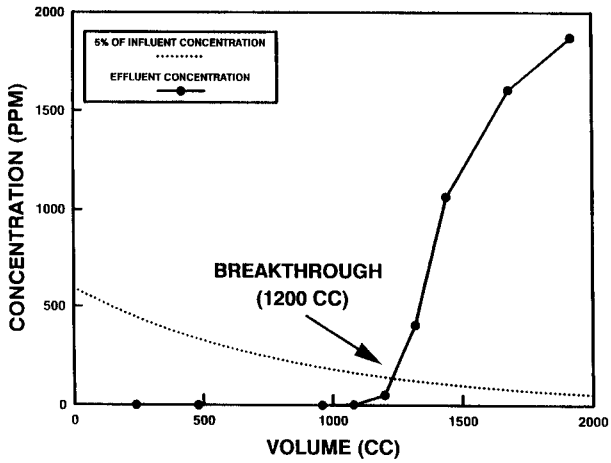

Figure 2. Pulsed breakthrough curve of chlorodifluoromethane from a 400/200-mg charcoal tube. The sampling flowrate was 25 cc/min, and 10.6 mg of chlorodifluoromethane were initially added to the charcoal.

PTFE/silicone septum, was placed on the vial and the vial was shaken gently. For precision and accuracy experiments, the front and back tubes were desorbed and analyzed separately. The resulting solutions were analyzed on the same day as desorption. For transfer of sample solutions into the syringe, the vial was inverted to allow the needle to come in contact with the charcoal, as provided in Method S111.

RESULTS AND DISCUSSION

Capacity experiments with the two sizes of charcoal tubes showed that chlorodifluoromethane required the larger sorbent bed to allow an adequate sampling time. Capacity experiments performed with generated atmospheres indicated that breakthrough of 5% of the chlorodifluoromethane occurred with the 100/50-mg charcoal tube after 20 min when sampling at 2× PEL. This indicated that the capacity was less than 0.5 L (see Figure 1). Yet, the 400/200-mg charcoal tube had an average capacity of 2.2 L, observed when breakthrough occurred at 85 and 55 min for sampling rates of 25 and 40 cc/min, respectively. To simulate possible short excursions to elevated concentrations, capacity was evaluated by another procedure, described elsewhere as the pulse method.[15] Analyte (3.5–10.6 mg) was added to the charcoal and then clean laboratory air was drawn through the tube to observe if and when the analyte would migrate from the charcoal. The breakthrough volume was determined by the intersection of the effluent concentration with a line representing 5% of the time-weighted influent concentration (Figure 2). This technique indicated capacities of 0.9–2.0 L for varying initial amounts of chlorodifluoromethane and sampling flowrates of 15–40 cc/min (Table I).

Gas chromatography with flame-ionization detection was the method of analysis for the NMAM methods. The chromatographic column recommended in NMAM Method 1018 was a stainless steel, 1.2 × 6 mm OD, packed with 80/100 mesh Chromosorb 102. For this evaluation two fused silica capillary columns were tested, a DB-WAX and a DB-1. Chlorodifluoromethane eluted as a split peak with severe tailing immediately before the solvent on the DB-WAX column (Figure 3). The DB-1 column provided an improved separation of chlorodifluoromethane from the solvent with good peak shape and was used for all analyses in this evaluation.

The use of carbon disulfide as the extraction solvent, as in NMAM Methods 1020 and 2516, was evaluated to observe solubility of the analyte. Standards of chlorodifluoromethane in carbon disulfide were prepared and then compared to standards in methylene chloride. The concentration of both sets of standards ranged from 0.1–0.8 mg/mL. The slope of a calibration curve prepared from the carbon disulfide solutions was lower than that obtained from methylene chloride solutions (28 vs. 49). Chlorodifluoromethane appeared to have the same limited solubility in carbon disulfide as documented for dichlorodifluoromethane and dichlorotetrafluoromethane.[8,9] Because of these capacity and solubility problems with NMAM Methods 1020 and

TABLE I. Pulse Method Breakthrough Data for 400/200-mg Coconut-Shell Charcoal Tube

Amount Added to Charcoal (mg)	*Sampling Flowrate (cc/min)*	*Apparent Concentration @ Breakthrough (mg/m³)*	*Breakthrough Volume (L)*
9.55	15	8680	1.1
9.77	25	8490	1.3
9.85	40	8210	1.2
6.52	40	5930	1.1
3.26	40	1630	2.0

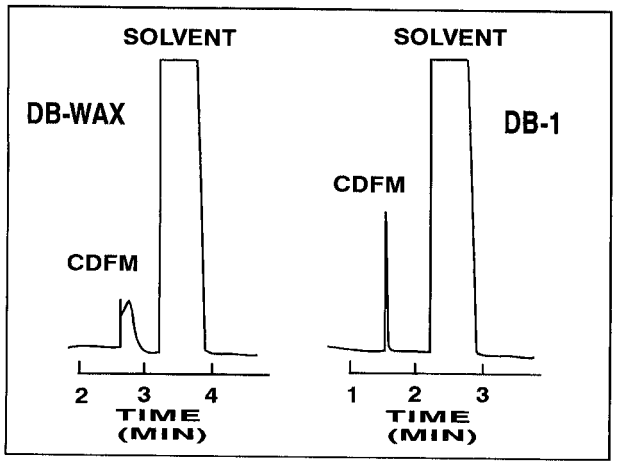

Figure 3. Chromatograms of chlorodifluoromethane on DB-1 and DB-WAX capillary columns

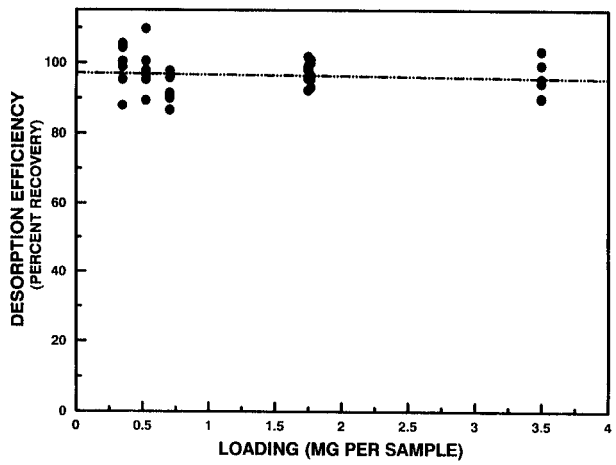

Figure 4. Desorption efficiency (percent recovered) of chlorodifluoromethane from activated charcoal (SKC lot 120) versus amount loaded. The regression line for the data is shown.

2516, these methods were determined to be unsuitable for chlorodifluoromethane.

Standard preparation procedures in NMAM Method 1018 weighed the solvent before and after adding analyte, using the difference as the correct amount. However, weighing a glass vial with cap and 20 mL of methylene chloride (ca. 46 g) accurately and precisely to five places was difficult. The variability of ± 1 mg was not adequate when trying to prepare standards of milligram quantities. Therefore, standards were prepared as described in NIOSH Method S111. Known quantities of chlorodifluoromethane, as determined from the measured volume of gas corrected to standard conditions, were added to 20-mL portions of methylene chloride. This procedure yielded reproducible linear calibration curves for chlorodifluoromethane.

It was expected that an amount of chlorodifluoromethane as low as 0.01 mg/sample could be distinguished from the background by gas chromatography. The limit of detection (LOD) and limit of quantitation (LOQ) were determined following standard operating procedures of our laboratory.[13] Six 400/200-mg tubes were fortified with amounts of analyte not exceeding 0.1 mg (10× expected LOD). The samples were desorbed with 20 mL of methylene chloride and analyzed the same day. Duplicate injections were made at each level, obtaining 12 responses for the construction of a calibration curve. The LOD was calculated as three times the standard error divided by the slope of this calibration curve. This calculation resulted in an LOD value of 0.007 mg per sample. Since no calibration standard was prepared as low as the calculated 0.007 mg of analyte, the LOD was reported as the lowest standard analyzed, 0.01 mg. The LOQ was calculated as 3.33× LOD, and was therefore determined to be 0.03 mg. To obtain an instrumental LOD, three dilutions of the lowest calibration standard solution (0.01 mg/20 mL of solution) were prepared (0.003, 0.005, and 0.008 mg/20 mL of solution) and analyzed. The six responses were added to the twelve mentioned above, and an analogous 0.01 mg of chlorodifluoromethane was distinguishable from the background.

TABLE II. Summary of Results from the Analyses of Generated Samples for the Evaluation of NMAM Method 1018 for the Determination of Chlorodifluoromethane

	0.5×PEL	1×PEL	2×PEL
Number of Samples Generated	6	6	6
Average Concentration Sampled (mg/m³)	1779	3315	6972
Average Concentration Found (mg/m³)[A]	1801	3512	6896
Percent Recovery	101.3	99.9	98.9
Coefficient of Variation (CV_2)	0.055	0.041	0.032

[A]Corrected for desorption efficiency.

Recovery of chlorodifluoromethane from charcoal was tested by directly introducing analyte to the 400/200-mg sorbent bed, extracting with 20 mL of methylene chloride, and quantitatively analyzing the resulting solutions. Five sets of six tubes with varying amounts of chlorodifluoromethane (0.53, 0.71, 1.77, 5.33 and 10.42 mg) were stored at ambient conditions for 18–24 hr before desorption. Results of the analyses showed acceptable losses of chlorodifluoromethane upon desorption. The recoveries ranged from 86–110%. The pooled average relative standard deviation (CV_1)[16] was 0.051. The recovery versus the amount of chlorodifluoromethane added to the charcoal is shown in Figure 4. An average desorption efficiency of 96.5% was used to calculate corrected amounts for precision and accuracy, and sample stability measurements.

Precision and accuracy of NMAM 1018 for chlorodifluoromethane were assessed by generation of test atmospheres at concentrations ranging from 0.5–2.0× PEL and collection of air using two charcoal tubes in-series for each sample. Six samples (12 tubes) were collected one at a time at each of three concentration levels, then stored at ambient conditions

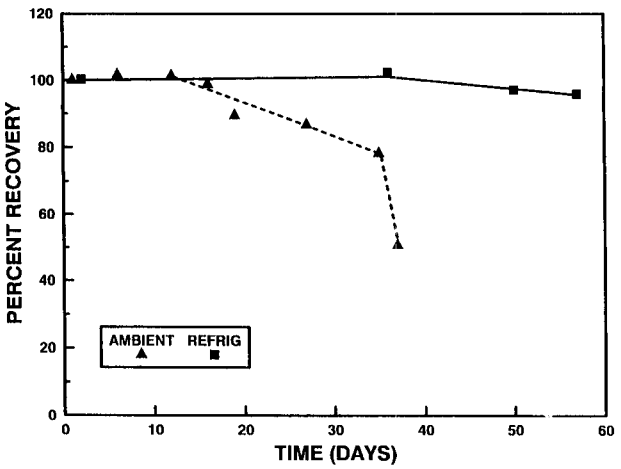

Figure 5. Sample storage stability of chlorodifluoromethane on charcoal at an average concentration of 3533 mg/m³ at 0° C and ambient temperature. Each point represents an average of three samples.

for 18–24 hours. The back tube was considered as the backup section of the total sorbent bed. On two 2× PEL-level samples, which had extended sampling times (greater than 60 min), analyte was detected on the backup sections. However, the amount on the backup tube was less than 1.5% of the amount found on the front tube. A summary of the results of the analysis of these samples is presented in Table II. The bias of the method was less than 2% at all three levels. The precision of these generated samples (CV_2),[16] calculated by pooling the relative standard deviations of the three sets of samples, was 0.043. Because CV_1 was less than CV_2, the total precision of the method, CV_T, was calculated as outlined in the Statistical Protocol for the NIOSH Validation Tests,[16] and determined to be 0.074.

Sample stability studies indicated that refrigeration is preferred for long-term storage of chlorodifluoromethane on charcoal. Although no loss of analyte was observed when samples were stored for 16 days under ambient conditions, more than 10% of the analyte was lost from samples stored under the same conditions for 19 days. When 24 samples collected at 1× PEL were stored at 0° C, less than 5% of the chlorodifluoromethane was lost after 57 days. The results of the sample stability evaluation are shown in Figure 5.

CONCLUSIONS

The purpose of this study was to evaluate NMAM Method 1020, 2516, and 1018 for the sampling and analysis of chlorodifluoromethane. NMAM Methods 1020 and 2516 were not suitable because the 100/50-mg charcoal tube had a limited capacity and chlorodifluoromethane had low solubility in carbon disulfide. NMAM Method 1018 was determined to be a suitable method for the quantitation of chlorodifluoromethane at the PEL (1000 ppm, 3500 mg/m³) and the NIOSH STEL (1250 ppm, 4375 mg/m³) when appropriate modifications were incorporated. These changes include using a capillary column for gas chromatographic analysis and preparing standards in an appropriate manner for a gas. A revised NMAM Method 1018 will include chlorodifluoromethane and will be published in the 4th edition of the NIOSH *Manual of Analytical Methods*.

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