METHOD 9057

DETERMINATION OF CHLORIDE FROM HCl/Cl_2 EMISSION SAMPLING TRAIN (METHODS 0050 AND 0051) BY ANION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method describes the analytical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chloride ($Cl_{2,}$ CAS Registry Number 7782-50-5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midget impinger HCl/Cl_2 sampling train (Method 0051) or the isokinetic sampling train (Method 0050).

1.2 The lower detection limit is 0.1 µg of chloride (Cl^-) per mL of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.

1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

2.0 SUMMARY OF METHOD

The stoichiometry of HCl and Cl_2 collection in the sampling train (see Methods 0050 and 0051) is as follows: In the acidified water absorbing solution, The HCl gas is solubilized and forms chloride ions (Cl-) according to the following formula:

$$HCl + H_2O = H_3O^+ + Cl^-$$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^- , and hypochlorous acid (HClO) as shown:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the Cl^-.

As part of Methods 0050 and 0051, sodium thiosulfate solution is added to the contents of the hydroxide filled impingers, in order to promote the following reaction.

$$S_2O_3^{-2} + 4OCl^- + 2OH^- = 2SO_4^{-2} + 4Cl^- + H_2O$$

Conversion of all the original Cl_2 to the stable Cl^- ion, and appropriate adjustment of the analysis calculations, removes the possibility of partial reduction of OCl^- to Cl^- and the resulting high bias to the results.

3.0 INTERFERENCES

Volatile materials which produce chloride ions upon dissolution during sampling are interferences in the sampling phase of the measurement of HCl emissions, but are not interferences in the Method 9057 analytical phase. Excessive amounts of other anions may cause interference in Method 9057 by "tailing" and other well known chromatographic effects. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.0 APPARATUS AND MATERIALS

4.1 Volumetric Flasks. Class A, various sizes, as appropriate.

4.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.

4.3 Ion Chromatograph. Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in the method refer to reagent water as specified by definition in Chapter One.

5.3 Sulfuric acid (0.1 N), H_2SO_4. To prepare 100 mL, slowly add 0.28 mL of concentrated H_2SO_4 to about 90 mL of water while stirring, and adjust the final volume to 100 mL using additional water. Shake well to mix the solution.

5.4 Sodium hydroxide (0.1 N), NaOH. To prepare 100 mL, dissolve 0.40 g of solid NaOH in about 90 mL of water and adjust the final volume to 100 mL using additional water. Shake well to mix the solution.

5.5 Reagent blank solutions. A separate blank solution of each sampling train regent used and collected in the field (0.1 N H_2SO_4 and 0.1 N NaOH) should be prepared for analysis with the field samples. For midget impinger train sample analysis, dilute 30 mL of each reagent with rinse water collected in the field as a blank to the final volume of the samples. For isokinetic train sample analysis, dilute 200 mL to the same final volume as the field samples also using the blank sample of rinse water.

5.6 Sodium chloride, NaCl, stock standard solution. Solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl that has been dried at 110°C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.0001 g, dissolve in water, and dilute to 1 liter. The exact Cl^- concentration can be calculated using the equation:

$$\mu g\ Cl^-/mL = g\ of\ NaCl \times 1000 \times 35.453/58.44$$

Refrigerate the stock standard solutions and store no longer than one month.

5.7 Chromatographic eluent. Effective eluent for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to a pH of 4.0 using a saturated sodium borate solution, and a mM 4-hydroxy benzoate solution, adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chloride peak, use a 2 mM sodium hydroxide/2.4 mM sodium bicarbonate eluent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING.

6.1 Sample collection using the midget impinger HCl/Cl_2 train or the isokinetic HCl/Cl_2 train is described in Method 0051 or 0050, respectively.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 PROCEDURE

7.1 Sample preparation for analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. For midget impinger train samples, quantitatively transfer each sample solution to a 100-mL volumetric flask and dilute to 100 mL with water. For isokinetic sampling train samples, quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume appropriate for all samples.

7.2 Calibration of Ion Chromatograph.

7.2.1 The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. Prior to calibration and sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present.

7.2.2 Prepare calibration standards to match the sample matrix by diluting given amounts (1.0 mL or greater) of the stock standard solution to convenient volumes using 0.1N H_2SO_4 or 0.1N NaOH, as appropriate. Prepare at least four standards that are within the linear range of the field samples. Inject the calibration standards, starting with the lowest concentration standard first.

7.2.3 Determine the peak areas, or heights, of the standards and plot individual values versus Cl^- concentrations in µg/mL. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve. The linear correlation coefficient must be $\geq$ 0.995.

7.3 Sample analysis. After calibrating the instrument, analyze in duplicate the quality control check sample, the reagent blanks, the field samples, and a matrix spike sample. Analyze the quality control check sample after every 10 samples, and at the end of the analysis period. Measure the areas or heights (whichever was used to prepare the linear regression curve) of the Cl^- peaks. Use the average response of the quality control check sample, field samples, matrix spike, and reagent blanks to calculate the concentrations using the linear calibration curve. The concentration of the quality control check sample determined from the calibration curve must be within 10% of the theoretical value. The results for a reagent blank must not exceed 10% of the corresponding value for the field samples.

7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.4.1 Total µg HCl per sample. Calculate as described below:

$$m_{HCl} = S \times V_s \times 36.46/35.45$$

where:

m_{HCl} = Mass of HCl in sample, µg
S = Analysis of sample, µg Cl^-/mL
V_s = Volume of filtered and diluted sample, mL
36.46 = Molecular weight of HCl, µg/µg-mole
35.45 = Molecular weight of Cl^-, µg/µg-mole

7.4.2 Total µg Cl_2 per sample. Calculate as described below:

$$m_{Cl2} = S \times V_2$$

where:
V_2 = Volume of filtered and diluted sample, mL
S = Analysis of sample, µg Cl^-/mL
m_{Cl2} = Mass of Cl_2 in sample, µg

7.4.3 Concentration of HCl in the flue gas: Calculate as described below:

$$C = K \times m/V_{m(std)}$$

where:

C = Concentration of HCl or Cl_2, dry basis, mg/dscm,
K = 10^{-3} mg/µg,
m = Mass of HCl or Cl_2 in sample, µg
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (from Method 0050 or Method 0051).

8.0 QUALITY CONTROL

8.1 At the present time, a validated audit material does not exist for the method. However, it is strongly recommended that a quality control check sample and a matrix spike sample be used.

8.1.1 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Institute of Science and Technology (SRM 3182). Prepare the QC check sample in the appropriate absorbing reagent (0.1N H_2SO_4 or 0.1N NaOH) at a concentration approximately equal to the mid-range calibration standard. Inject the QC check sample in duplicate immediately after the calibration standards, after every 10 samples, and at the end of the analysis period. The Cl^- value obtained for the check sample using the final calibration curve must be within 10% of the known value for the check sample. If the check sample is outside this limit, recalibrate, and reanalyze any samples following the last successful check sample analysis.

8.1.2 Matrix spike sample. A portion of at least one field sample should be used to prepare a matrix spike sample. Spike the sample aliquot in the range of the expected concentration. Analyze the matrix spike sample in duplicate along with the field samples. Based on the matrix spike results, determine the recovery for the spiked material. This should be within 10 percent of the known spike value.

8.2 Refer to Chapter One for additional quality control criteria.

9.0 METHOD PERFORMANCE

9.1 The lower detection limit of the analytical method is 0.1 µg of Cl^- per mL of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

9.2 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl_2 train (Method 0051) for sample collection. The within-laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

10.0 REFERENCES

1. Steinsberger, S.C. and J. H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB89 220586-AS.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources" March 18, 1987.

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

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