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CHLORINE EMISSIONS FROM HAZARDOUS WASTE INCINERATORS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

APR 19 1990

MEMORANDUM

SUBJECT: Chlorine Emissions from Hazardous Waste Incinerators

FROM: Matthew Hale, Acting Director  
Permit and State Programs Division (OS-343)

TO: William Honker, Chief  
RCRA Permits Branch (6H-P)  
Region VI

This is in response to your March 13, 1990, memorandum suggesting the need to control chlorine emissions from hazardous waste incinerators and requesting interim guidance on chlorine emission control and measurement.

As mentioned at the last Incinerator Permit Writers Workgroup Meeting, EPA is requesting comments on a proposal to amend 264.343(b) so that the existing 99% removal standard would apply to both hydrogen chloride (HCL) and free chlorine. EPA is also proposing to require a health-based check to ensure that the technology-based standard for free chlorine is protective. Accordingly, the applicant would be required to demonstrate that the Maximum Exposed Individual (MEI) is not exposed to free chlorine emissions exceeding the proposed annual average reference air concentration (RAC) of 0.4 micrograms per cubic meter. This amendment is included in the proposed incinerator regulations signed by the Administrator on April 9, 1990. A copy of that proposal was sent to your Division Director under separate cover.

As indicated in the proposed incinerator regulations, compliance with the health-based chlorine standard would be demonstrated by: (1) emissions testing and dispersion modelling; (2) emission testing and conformance with the chlorine emission screening limits; or (3) waste analysis and conformance with

chlorine feed rate screening limits. the emission and feed rate screening limits for chlorine can be determined by multiplying 1.33 times the corresponding limits established for mercury in Appendix E of the boiler/furnace supplemental notice (see 54 FR 43745). If emission testing for chlorine is required, the "Draft Method for Determination of HCL Emissions from Municipal and Hazardous Waste Incinerators" should be used (see attachment).

As with the proposed controls for metals and HCl, the permit writer can exercise his authority under Section 3005(c)(3) of RCRA to develop permit requirements as may be necessary to ensure that chlorine emissions do not pose unacceptable health risk to human health and the environment. If you have any further questions on this matter, please contact Lionel Vega of my staff at FTS 475-8988.

Attachment

cc: Elizabeth Cotsworth  
Sonya Stelmack  
Lionel Vega  
Shiva Garg

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MIDGET IMPINGER HC1/C12 EMISSION SAMPLING TRAIN

DRAFT

This method has been drafted based on the results of laboratory and field studies carried out under contract to the Source Branch of the Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory (QAD/AREAL), United States Environmental Protection Agency (U.S. EPA). The method is still under investigation and is subject to revision.

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## MIDGET IMPINGER HCl/Cl<sub>2</sub> EMISSION SAMPLING TRAIN

### 1.0 SCOPE AND APPLICATION

1.1. This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl<sub>2</sub>, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method XXXX. This method is designed to collect HCl/Cl<sub>2</sub> in their gaseous forms. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl<sub>2</sub> sampling train (see Method XXXX).

### 2.0 SUMMARY OF METHOD

2.1 An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl<sup>-</sup>) ions. The Cl<sub>2</sub> 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<sup>+</sup>), Cl<sup>-</sup>, and hypochlorous acid (HOCl). The Cl<sup>-</sup> ions in the separate solutions are measured by ion chromatography (Method XXXX).

### 3.0 INTERFERENCES

3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferent for HCl is diatomic chlorine (Cl<sub>2</sub>) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl<sub>2</sub> gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl<sub>2</sub> with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl<sub>2</sub> results in a positive bias of 3.4% in the HCl measurement.

### 4.0 APPARATUS AND MATERIALS

4.1 Sampling Train. The sampling train is show in Figure 1 and component parts are discussed below.

4.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in. (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe; a 1-in. (25-mm) length of Teflon tubing with a 3/8-in.

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4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F).

4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

4.2 Sample Recovery.

4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

## 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 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method XXXX).

5.3 Sulfuric acid (0.1 N), H<sub>2</sub>SO<sub>4</sub>. used as the CHI absorbing reagent. to prepare 100 mL, slowly add 0.28 mL of concentrated H<sub>2</sub>SO<sub>4</sub> 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. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method XXXX).

5.4 Sodium hydroxide (0.1 N), NaOH. Used as the Cl<sub>2</sub> absorbing reagent. 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

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7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in Section 7.1.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

7.1.3 Rate meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

## 7.2 Sampling.

7.2.1. Preparation of collection train. prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midjet impingers should each be filled with 15 mL of 0.1 N H<sub>2</sub>SO<sub>4</sub>, and the fourth and fifth impingers should each be filled with 15mL of 0.1 N NaOH. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest 0.5 g and record

the weight.

7.2.2 Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. the vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 250°F and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to

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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 Nomenclature.

Bws = Water vapor in the gas stream, proportion by volume.

Mw = Molecular weight of water, 18.0 g/g-mole  
(18.0 lb/lb-mole).

Pbar = Barometric pressure at the exit orifice of the dry gas  
meter, mm Hg (in. Hg).

Pstd = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m<sup>3</sup>/°K-g-mole  
(21.85 in. Hg-ft<sup>3</sup>/°R-lb-mole).

Tm = Average dry gas meter absolute temperature, °K (°R).

Tstd = Standard absolute temperature, 293°K (528°R).

Vlc = Total volume of liquid collected in impingers and silica  
gel, mL (equivalent to the difference in weight of the  
impinger train before and after sampling, 1 mg = 1 mL).

Vm = Dry gas volume as measured by the dry gas meter, dcm  
(dcf).

Vm(std) = Dry gas volume measured by the dry gas meter, corrected  
to standard conditions, dscm (dscf).

Vw(std) = Volume of water vapor in the gas sample, corrected to  
standard conditions, scm (scf).

Y = Dry gas meter calibration factor.

Pw = Density of water, 0.9982 g/mL (0.002201 lb/mL).

7.4.2. Sample volume, dry basis, corrected to standard conditions.  
 Calculate as described below:

$$V_m(\text{std}) = V_m \cdot Y \cdot \frac{T_{\text{std}}}{T_m} \cdot \frac{P_{\text{bar}}}{P_{\text{std}}} = K_1 \cdot Y \cdot \frac{V_m P_{\text{bar}}}{T_m}$$

where:

$K_1 = 0.3858^\circ\text{K}/\text{mm Hg}$  for metric units.  
 $= 17.64^\circ\text{R}/\text{in. Hg}$  for English units.

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5. U. S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Method  
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PROTOCOL FOR ANALYSIS OF SAMPLES  
FROM HCl/Cl<sub>2</sub> EMISSION SAMPLING TRAINS

DRAFT

This method has been drafted based on the results of laboratory and field studies carried out under contract to the Source Branch of the Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory (QAD/AREAL), United States Environmental Protection Agency (U.S. EPA). The method is still under investigation and is subject to revision.

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. ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sulfuric acid (0.1 N), H<sub>2</sub>SO<sub>4</sub>. To prepare 100 mL, slowly add 0.28 mL of concentrated H<sub>2</sub>SO<sub>4</sub> 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 reagent used and collected in the field (0.1 N H<sub>2</sub>SO<sub>4</sub> and 0.1 N NaOH) should be prepared for analysis with the field samples. For midjet 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 100°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 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl<sup>-</sup> concentration can be calculated using the equation:

$$\mu\text{g Cl}^- / \text{mL} = \text{g of NaCl} \times 10^3 \times 35.453 / 58.44$$

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

5.7 Chromatographic effluent. Effective eluents 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-dihydroxy benzoate solution.

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7.2.3 After injecting the standards the first time, determine the peak area or height for each standard. Using linear regression, determine the equation for the calibration curve. Compare the known concentration of each standard to its concentration predicted by the calibration equation; the percent error as calculated below should be less than or equal to 7 percent.

$$\% \text{ Error} = \frac{\text{Predicted Conc.} - \text{Known Conc.}}{\text{Known Conc.}} \times 100\% \quad (1)$$

7.2.4 Following analysis of the quality control sample, the reagent blanks, and the field samples, the calibration standards are injected a second time.

7.2.5 Using the average of the initial and final injections of the standards and linear regression, determine the formulas for the calibration curve to be used to calculate the field sample concentrations.

7.3 Sample analysis. Between injections of the series of calibration standards, inject in duplicate the reagent blanks and the field samples, including a matrix spike sample. measure the areas or heights (same as done for the calibration standards) of the Cl<sup>-</sup> peaks. Each response (peak height or area) for a duplicate injection should be within 5 percent of the average response. Using the average response to determine the concentrations of the field samples, matrix spike, and reagent blanks using the linear calibration curve. The results for a reagent blank shall not exceed 10 percent of the corresponding value for a field sample.

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 ug HCl per sample. Calculate as described below:

$$m\text{HCl} = (S-B) \times V_s \times 36.46/35.453 \quad (2)$$

where: mHCl = Mass of HCl in sample, ug,

S = Analysis of sample, ug Cl<sup>-</sup>/mL

B = Analysis of reagent blank, ug Cl<sup>-</sup>/mL,

$V_s$  = Volume of filtered and diluted sample, mL,  
36.46 = Molecular weight of HCl, ug/ug-mole, and  
35.453 = Atomic weight of Cl, ug/ug-mole.

7.4.2 Total ug Cl<sub>2</sub> per sample. Calculate as described below:

$$MC_{12} = (S-B) \times V_s \times 70.90/35.45 \quad (3)$$

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respectively. The method does not exhibit any bias for HCl when sampling at Cl<sub>2</sub> concentrations less than 50 ppm.

#### 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. \_\_\_\_\_ , \_\_\_\_\_ , 1989.
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.