

State of California
Air Resources Board

Method 434

Determination of Chlorine in Unheated Air

Adopted: September 12, 1990

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INTRODUCTION

This method is an adaptation of methodology identified as method number P&CAM 209 in NIOSH Manual of Analytical Methods, 2nd Ed., Part 1 - NIOSH Monitoring Methods, Volume 1, published by the U.S. Department of Health, Education and Welfare in April, 1977.

1 APPLICABILITY AND PRINCIPLE

1.1 Applicability

These procedures are intended for use in measurement of gaseous chlorine (Cl_2) concentration in unheated air vented from or exposed to processes and facilities using either aqueous chlorine (or hypochlorite) solutions or compressed or liquid chlorine. Although suitability for measurement of chlorine in combustion exhaust or other non-air gas streams (other situations) has not been demonstrated, the Executive Officer may approve this method for other situations if data are submitted demonstrating that the method is applicable. The apparatus specified is not considered suitable for heated gas streams containing substantial amounts of condensable water or entrained particulate matter.

1.2 Principle

Chlorine is absorbed from a metered volume of air by an acidified methyl orange solution in a bubbler, reacting with the methyl orange to produce a color change which is measured by colorimetry. The presence of excess methyl orange enhances absorption of chlorine. Acidification brings pH of the solution into a range where its variations do not affect solution color.

2 RANGE AND SENSITIVITY

These procedures are intended to cover a range of chlorine concentrations equivalent to 5 to 100 micrograms of chlorine per 100 mL of sampling solution, corresponding approximately to 0.05 to 1.00 ppmv in a 30 L air sample. Chlorine free air produces some color shift and large increases in sampling time are not a practical way of extending sensitivity.

3 INTERFERENCES

Interferences from manganese compounds, bromine, nitrogen dioxide, and possibly ozone can lead to overestimation of the amount of chlorine. Nitrites can discolor the absorbing solution. Sulfur dioxide can lead to underestimation of the amount of chlorine. As noted above, chlorine free air has some bleaching effect on the absorbing solution and large sample sizes may lead to borderline false positives.

4 APPARATUS

All apparatus which comes in contact with sampled gas or solutions shall be of glass or other substantially unreactive and impermeable material. Joints shall be sealed with silicone grease and/or substantially impermeable and unreactive elastomers.

4.1 Sampling Apparatus

- 4.1.1 Sample line of Teflon tubing with provision for plugging or valving off the inlet end during leak test.
- 4.1.2 Two Greenberg-Smith type glass impingers, 250 to 350 mL fluid capacity, modified to discharge gas from the downtube through a coarse glass frit.
- 4.1.3 Two unmodified Greenberg-Smith impingers or one impinger and a silica gel cartridge.
- 4.1.4 Rotameter capable of measuring flow rates of up to 2 L of air per minute.
- 4.1.5 Sample pump, gas tight, with throttling and bypass valves as necessary to adjust flow rate to 1.5 L/min.
- 4.1.6 Dry gas meter capable of measuring gas volume accurately at flow rates of 1.5 L/min and equipped with temperature compensation or with inlet and outlet thermometers.
- 4.1.7 Miscellaneous fittings and connectors to assemble and support above components.

4.2 Analytical Apparatus

- 4.2.1 Spectrophotometer suitable for measurement of absorbance at 505 nanometer and accommodating five cm absorption cells.
- 4.2.2 Glassware including burette with stopcock and supporting stand for titrations, solution storage bottles with airtight screw caps, volumetric flasks (1.000 L and 100 mL), graduated cylinder (100 or 150 mL and 10 mL), beakers, and graduated pipet (10 mL).

5 REAGENTS AND MATERIALS

Reagents should be ACS analytical grade quality. Distilled water should conform

to ASTM Standard for Referee Reagent Water.

5.1 Chlorine-demand-free Distilled Water.

5.1.1 Distilled water required in reagent preparation and sampling should be free of chlorine demand.

5.1.2 Chlorine-demand-free distilled water may be prepared as follows. Add chlorine to distilled water to destroy the ammonia, at least ten times the amount of ammoniacal nitrogen present and sufficient to produce an initial chlorine residual of no less than 1.0 mg/L free chlorine. Allow the chlorinated distilled water to stand overnight or longer, then expose to direct sunlight or a UV lamp for 1 day or until all residual chlorine is discharged.

5.2 Methyl Orange Stock Solution, 0.05%

Dissolve 0.500 g reagent grade methyl orange (4-[p-(dimethylamino)phenylazo] benzenesulfonic acid sodium salt) in distilled water and dilute to 1 L; use freshly boiled and cooled distilled water.

5.3 Methyl Orange Reagent, 0.005%

Dilute 100 mL of stock solution to 1000 mL; prepare fresh daily.

5.4 Sampling Solution.

Dilute 6 mL of 0.005% Methyl Orange reagent to 100 mL and add 3 drops (0.15 - 0.20 mL) 5N HCl. 1 drop of butanol may be added to enhance foaming at the option of the tester.

5.5 Acidified Water

To 100 mL of distilled water add 3 drops of 5N HCl.

5.6 Potassium Dichromate Solution, 0.1000 N

Dissolve 4.904 g anhydrous $K_2Cr_2O_7$, primary standard grade, in distilled water and dilute to 1 L.

5.7 Starch Indicator Solution

Prepare a thin paste of 1 g of soluble starch in a few mL of distilled water, bring 200 mL of distilled water to a boil and remove from heat, and stir in the starch paste. Prepare fresh daily.

5.8 Potassium Iodide, reagent grade.

5.9 Sodium Thiosulfate Solution, 0.1 N, Standardized against Potassium Dichromate.

Dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled and cooled distilled

water and dilute to 1 L. Add 5 mL chloroform as preservative and allow to age for two weeks before standardizing. Add, with constant stirring, to 80 mL of distilled water: 1 mL concentrated H₂SO₄, 10.00 mL of 0.1000 N K₂Cr₂O₇, and approximately 1 g of KI; let stand 6 minutes in the dark. Titrate the mixture with the aged thiosulfate stock solution; when a color change from brown to yellowish green indicates the endpoint is near add 1 mL of starch indicator solution and continue titrating until a color change from blue to light green indicates the endpoint has been reached.

- 5.10 Sodium Thiosulfate Solution, 0.01 N
Dilute 100 mL of the aged and standardized Na₂S₂O₃ solution to 1000 mL with freshly boiled and cooled distilled water. Add 5 mL chloroform as a preservative. Standardize frequently, or on the day used, with 0.0100 N K₂Cr₂O₇.
- 5.11 Chlorine Solution, approximately 10 mg/L
Prepare fresh by serial dilution of household chlorine bleach; assume a concentration of 50000 mg/L in the bleach and dilute 5000 to 1 with distilled water. Alternatively, prepare fresh by dilution of strong chlorine water made by bubbling chlorine gas through cold water.
- 5.12 Potassium Dichromate Solution, 0.0100 N
On the day of use fill a 100 mL volumetric flask to volume with 0.1000 N potassium dichromate solution, transfer to a 1000 mL volumetric flask, rinse the smaller flask into the larger and make to volume with distilled water.
- 5.13 Glacial Acetic Acid, reagent grade

6 PRETEST PREPARATIONS

Prepare all solutions and reagents described in the reagent section except the chlorine solution.

7 SAMPLING AND ANALYSIS

- 7.1 Assemble Sample Train
Mark the two frit-equipped impingers as #1 and #2, mark an unmodified impinger #3, and mark a final impinger or silica gel cartridge #4. Measure 100 mL of sampling solution into impingers #1 and #2. Leave the #3 unmodified impinger empty. Add fresh silica gel to the fourth impinger or cartridge. Connect in sequence so that sampled gas will enter through impinger #1 and exit through #4 to the rotameter and thence the dry gas meter and sample pump. Arrange an ice bath to cool only impingers #3 and #4 (the empty impinger and the silica gel) and not impingers #1 and #2.

7.2 Leak Test Sample Train

Plug the intake end of the sample line and start the sample pump. If any continuing flow is indicated by the rotameter or dry gas meter, locate and correct leaks and repeat the leak check. When releasing vacuum on the sample train unplug or open the sample line slowly, then promptly stop pump; avoid surges or reverse flow through impingers which can cause loss of liquid.

7.3 Sampling

Place intake end of sample line at a representative sampling location and support in position as necessary.

Record initial reading of the dry gas meter before starting sample pump.

Start the sample pump and adjust flow rate to 1.5 L/min as indicated by the rotameter.

Continue sampling for 20 minutes, passing approximately 30 L of sampled air through the impingers.

Stop the sample pump and record final reading on the dry gas meter.

7.4 Analysis

Analysis and calibration should be performed on site within one hour of completion of sampling.

Pipet sampling solution from impingers #1 and #2 into separate absorption cells and measure absorbance of each at 505 nm against distilled water as a reference using the spectrophotometer. Promptly calibrate the spectrophotometer.

7.5 Calibration

Prepare a series of colorimetric standards as follows.

To each of five labeled 100 mL volumetric flasks add 6 mL of the 0.005% methyl orange reagent, 75 mL of distilled water, and 3 drops (0.15 to 0.20 mL) of 5N HCl. Carefully and accurately pipet 0, 0.5, 1.0, 5.0 and 9.0 mL of the approximately 10 mg/L chlorine solution (see section 5.11) into different flasks with corresponding labels, holding the pipet tip below the surface to avoid chlorine loss. Quickly mix and fill to the volume mark with distilled water.

Immediately standardize the chlorine solution as follows: To a flask add 1 g KI, 5 mL of glacial acetic acid, and 400 mL of the chlorine solution;

stopper and swirl to mix. Titrate with 0.01 N Na₂S₂O₃: when the iodine color becomes a faint yellow, add 1 mL of starch indicator solution and continue the titration to the endpoint (blue to colorless transition).

Transfer each of the colorimetric standards to an absorption cell and measure its absorbance at 505 nm against distilled water as a reference using the spectrophotometer. Construct a calibration curve of absorbance vs chlorine concentration in mg/mL.

8 QUALITY ASSURANCE

Method performance should be demonstrated by sampling and analyzing an independently known mixture of chlorine in air, approximately 0.5 ppmv.

This "audit" mixture should be generated or blended immediately before or during use since stability of such mixtures is poor. Permeation tube systems and electrochemical chlorine generation systems are available for preparing audit mixtures. The method of generating the audit mixture is deliberately unspecified.

Results of analyzing an audit material are not to be used for calibration or as the basis for adjustment of emissions test results. Divergence of audit results from expected value indicates a defect in either method performance or the audit material and should be investigated accordingly.

An audit as described above should be performed in connection with each test or group of tests at a site unless statistical evidence indicates less frequent checks are adequate.

9 CALCULATIONS

Normality of Potassium Dichromate Solution

$$\text{Normality K}_2\text{Cr}_2\text{O}_7 = \frac{(\text{g dissolved in 1L})}{(49.04 \text{ g})}$$

Number of Equivalents of Potassium Dichromate Titrated, n

$$n = \frac{(\text{Normality K}_2\text{Cr}_2\text{O}_7) * (\text{mL K}_2\text{Cr}_2\text{O}_7 \text{ soln. added})}{1000}$$

Thiosulfate Standardization

$$\text{Normality of Na}_2\text{S}_2\text{O}_3 = \frac{(n * 1000)}{(\text{mL of Na}_2\text{S}_2\text{O}_3 \text{ added})}$$

Chlorine Solution Standardization

$$\text{chlorine mg/mL} = \frac{35.46 * N_{\text{thio}} * V_{\text{thio}}}{400}$$

where:

35.46 = chlorine mg/mL in a 1.0000 N solution

V_{thio} = mL $\text{Na}_2\text{S}_2\text{O}_3$ solution added

N_{thio} = normality of $\text{Na}_2\text{S}_2\text{O}_3$ used

400 = mL of chlorine solution titrated

Emissions Concentration, Cl_2 ppmv

Find total ppmv of Cl_2 in sampled air by adding ppmv for both impingers, i.e. total ppmv = ppmv₁ + ppmv₂. Find ppmv for each individual impinger as follows:

$$\text{Cl}_2 \text{ ppmv} = \frac{C_i * 10^3 * 100 * (24.45 / 70.92)}{V_{\text{air}}}$$

where:

C_i = chlorine mg/mL in impinger from calibration curve and measured absorbance

10^3 = 10^6 ppmv/(L/L) * 10^{-3} g/mg

100 = mL of methyl orange solution in impinger

24.45 = L/g-mole of Cl_2 at 760 mmHg, 25 deg. C

70.92 = g/g-mole of Cl_2

V_{air} = L of air sampled, corrected to 760 mmHg, 25 deg. C

Mass Emissions Rate LBH, lb/hour

$$\text{LBH} = \frac{60 * Q_{\text{std}} * 70.92 * \text{Cl}_2 \text{ ppmv} * 10^{-6}}{385.32}$$

where:

60 = min/hour

- Q_{std} = stack gas flow in dry cubic feet per minute at 68F and 1 atm as determined using ARB Methods 1, 2, 3, and 4
- 385.32 = volume in cubic feet of one pound-mole of gas at 1 atm, 68F (760 mmHg, 25 deg. C)
- 70.92 = lb of Cl_2 per lb-mole of Cl_2
- Cl_2ppmv = Cl_2 parts per million by volume
- 10^{-6} = (moles Cl_2 per mole air) / ppmv Cl_2 in sampled air

Impinger Penetration Criterion

If $ppmv_2$ is more than 25% of $ppmv_1$ consider impinger penetration unacceptably high and invalidate the test.

10 EQUIVALENT METHODS

The Executive Officer may approve alternate methods based on review of information demonstrating that the alternate methods produce results equivalent to this method.