

**DETERMINATION OF CHLORINE AND CHLORINE DIOXIDE IN
PULP MILL BLEACH PLANT VENTS**

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DETERMINATION OF CHLORINE AND CHLORINE DIOXIDE IN PULP MILL BLEACH PLANT VENTS

1.0 Introduction

This method was developed for measuring chlorine (Cl_2) and chlorine dioxide (ClO_2) in pulp mill bleach plant vents, and has proven to be effective when the concentrations of both compounds are close to the same order of magnitude in the gas stream being sampled. Due to the chemistry involved, the precision of the chlorine analysis will decrease as the ratio of chlorine dioxide to chlorine increases. Conversely, but to a lesser extent, the precision of the chlorine dioxide analysis will decrease as the ratio of chlorine dioxide to chlorine decreases. Slightly negative calculated concentrations of chlorine may occur when sampling a vent gas with high concentrations of chlorine dioxide and very low concentrations of chlorine. Because of these issues, there is some concern that as bleach plants eliminate the use of chlorine as a bleaching chemical, there may be some problems in accurately measuring low levels of chlorine in the presence of high concentrations of ClO_2 . Further studies to address this concern are planned.

2.0 Method Description

2.1 Principle, applicability, interferences, and stability

2.1.1 Principle - A gas sample is extracted from a bleach plant process vent and passed through impingers containing buffered potassium iodide solution. Post-sampling determination of iodine formed at neutral and acidic pH permits the quantitative measurement of both Cl_2 and ClO_2 .

2.1.2 Applicability - This method is applicable for the measurement of the concentration of chlorine (Cl_2) and chlorine dioxide (ClO_2) in pulp mill bleach plant and chlorine dioxide generator vents. Bias and precision were found to be acceptable when the method was evaluated according to EPA protocol.

2.1.3 Interferences - Known interfering agents of this method are sulfur dioxide and hydrogen peroxide. Sulfur dioxide (SO_2), which is used to reduce oxidant residuals in some bleach plants, reduces formed iodine to iodide in the capture solution. It is therefore a negative interference for chlorine, and in some cases could result in erroneous negative chlorine concentrations. Any agent capable of reducing iodine to iodide could interfere in this manner. A chromium trioxide impregnated filter will capture SO_2 and pass Cl_2 and ClO_2 (see References). Hydrogen peroxide, which is commonly used as a bleaching agent in modern bleach plants, reacts with iodide to form iodine (as does chlorine) and thus can cause a positive interference in the chlorine measurement.

Sunlight can cause photochemical degradation of ClO₂, so care should be made to shield the sampling train from light. Further discussion of these interferences can be found in this method's reference section.

- 2.1.4** Stability - Samples should be titrated within an hour of collection. If this is not possible, they should be chilled and stored in the dark for no more than 24 hours prior to analysis.

2.2 Apparatus

- 2.2.1** Sampling apparatus - A diagram of the sampling train is shown in Figure 1.

- 2.2.1.1** Probe/sampling line - A separate probe is not required. The sampling line consists of an appropriate length of 0.64 cm (0.25 in) OD Teflon tubing. The sample inlet end of the sampling line is inserted into the stack in such a way as to not entrain liquid condensation from the vent gases. The other end is connected to the impingers. The length of the tubing may vary from one sampling site to another, but should be as short as possible in each situation. If sampling is conducted in sunlight, opaque tubing should be used. Alternatively, if transparent tubing is used, it should be covered with opaque tape.
- 2.2.1.2** Impinger train - Three 30 mL capacity midget impingers are connected in series to the sampling line. The impingers should have regular tapered stems. Silica gel is placed in the third impinger as a desiccant. All impinger train connectors should be glass and/or Teflon.
- 2.2.1.3** Filter - A 45 mm diameter in-line Teflon 0.8 µm filter follows the impingers to protect the critical orifice and pump.
- 2.2.1.4** Rotameter - A 250 mL/min capacity rotameter is placed in line after the filter apparatus for a visual flow check during sampling and leak checking.
- 2.2.1.5** Critical orifice - The filter is connected to a 200-250 mL/min critical orifice.
- 2.2.1.6** Vacuum pump - The critical orifice is followed by a pump capable of providing a vacuum of 640 mm of Hg.
- 2.2.1.7** Flowmeter - A bubble tube flowmeter is used to measure flow at the sampling line tip prior to and after sampling.
- 2.2.1.8** A 20 mL pipette and dispensing bulb.

2.2.1.9 Thermometer - An accurate thermometer is used to measure ambient temperature.

2.2.1.10 Barometer - A barometer is used to measure barometric pressure.

2.2.2 Analysis apparatus

2.2.2.1 Wash bottle filled with deionized water.

2.2.2.2 A 25 or 50 mL graduated burette and stand.

2.2.2.3 Magnetic stirring apparatus and stir bar.

2.2.2.4 A calibrated pH meter.

2.2.2.5 A 150-250 mL beaker or flask

2.2.2.6 A 5 mL pipette.

2.3 Reagents

2.3.1 Water - Deionized water is to be used in making all reagents for this method.

2.3.2 Potassium dihydrogen phosphate solution, 1 M - Dissolve 13.61 g KH_2PO_4 in water and dilute to 100 mL.

2.3.3 Sodium hydroxide solution, 1 M - Dissolve 4.0 g NaOH in water and dilute to 100 mL.

2.3.4 Buffered 2% potassium iodide solution - Dissolve 20 g KI in ca. 900 mL water. Add 50 mL of 1 M KH_2PO_4 and 30 mL 1 M NaOH. While stirring solution, measure pH of solution electrometrically and add 1 M NaOH to bring pH to between 6.95 and 7.05.

2.3.5 Sodium thiosulfate solution, 0.01 N - First prepare 0.1 N sodium thiosulfate solution by dissolving 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ with freshly boiled and cooled distilled water in a 1 L volumetric flask. Dilute to volume. Standardize with potassium bi-iodate as in Standard Methods 4500-Cl B. To prepare 0.01 N sodium thiosulfate solution, add 10.0 mL standardized 0.1 N sodium thiosulfate solution to a 100 mL volumetric flask, and dilute to volume with water.

2.3.6 Sulfuric acid solution, 10% - Add 10 mL concentrated H_2SO_4 to ca. 80 mL water in an 100 mL volumetric flask. Dilute to volume.

2.4 Procedure

2.4.1 Sampling

- 2.4.1.1** Measure ambient temperature and barometric pressure.
- 2.4.1.2** Preparation of collection train - Measure 20 mL buffered potassium iodide solution into each of the first two impingers and connect probe, impingers, filter, critical orifice, and pump as in Figure 1. The sampling line and the impingers should be shielded from sunlight.
- 2.4.1.3** Leak and flow check procedure - Plug sampling line inlet tip and turn on pump. If a flow of bubbles is visible in either of the liquid impingers, tighten fittings and adjust connections and impingers. A leakage rate not in excess of 2% of the sampling rate is acceptable. Carefully remove the plug from the end of the probe. Check the flow rate at the probe inlet with a bubble tube flowmeter. The flow should be comparable or slightly less than the flow rate of the critical orifice with the impingers off-line. Record the flow and turn off the pump.
- 2.4.1.4** Sample collection - Insert the sampling line into the stack and secure it with the tip slightly lower than the port height. Start the pump, recording the time. End the sampling after 60 minutes, or sooner if the color in the second impinger turns from a pale yellow to a medium yellow. Record time and remove the tubing from the vent. Recheck flow rate at sampling line inlet and turn off pump. If the flow rate has changed significantly, redo sampling with fresh capture solution. A slight variation (<5%) in flow can be averaged. With the inlet end of the line elevated above the impingers, add about 5 mL water into the inlet tip to rinse the line into the first impinger.
- 2.4.1.5** Sample analysis - Fill the burette with 0.01 N sodium thiosulfate solution to the zero mark. Combine the contents of the impingers in the beaker or flask. Stir the solution and titrate with thiosulfate until the solution is colorless. Record the volume of the first endpoint (T_N , mL). Add 5 mL of the 10% sulfuric acid solution, and continue the titration until the contents of the flask are again colorless. Record the total volume of titrant required to go through the first and to the second endpoint (T_A , mL).

It is important that sufficient lighting be present to clearly see the endpoints, which are determined when the solution turns from pale yellow to colorless. A lighted stirring plate and a white background are useful for this purpose.

2.5 Calibration - Not applicable to this method.

2.6 Calculations

2.6.1 Nomenclature and calculations - Perform the calculations as follows:

Equation 1

Calculation of sample flow rate corrected to a dry basis:

$$S_C = S_U \left(\frac{BP - PW}{760} \right) \left(\frac{293}{273 + t} \right)$$

where:

S_C = Corrected (dry standard) sampling flow rate, L/min;

S_U = Uncorrected sampling flow rate, L/min.

BP = Barometric pressure at time of sampling.

PW = Saturated partial pressure of water vapor, mm Hg at *t*.

t = Ambient temperature, °C

Equation 2

Equivalents of iodine determined in neutral titration (EqI₂N):

$$EqI_2N = (T_N)(10^{-3})(N_{Thio})$$

Equation 3

Equivalents of iodine determined in (total) acid titration (EqI₂A):

$$EqI_2A = (T_A)(10^{-3})(N_{Thio})$$

Equation 4

$$\text{Moles } Cl_2 = 1/8 (5 EqI_2N - EqI_2A)$$

$$= 1/8000 (5 T_N - T_A) \times N_{Thio}$$

Equation 5

$$\begin{aligned} \text{Conc. Cl}_2 \text{ (ppm)} &= \frac{\text{Cl}_2 \text{ Moles} \times 24.04 \text{ L/mole} \times 10^6}{S_C \times t_S} \\ &= \frac{(5 T_N - T_A) \times N_{\text{Thio}} \times 24.04 \times 10^6}{8000 \times S_C \times t_S} \\ &= \frac{3005 (5 T_N - T_A) \times N_{\text{Thio}}}{S_C \times t_S} \end{aligned}$$

Equation 6

$$\begin{aligned} \text{Moles ClO}_2 &= 1/4 (EqI_2A - EqI_2N) \\ &= 1/4000 (T_A - T_N) \times N_{\text{Thio}} \end{aligned}$$

Equation 7

$$\begin{aligned} \text{Conc. ClO}_2 \text{ (ppm)} &= \frac{\text{ClO}_2 \text{ Moles} \times 24.04 \text{ L/mole} \times 10^6}{S_C \times t_S} \\ &= \frac{(T_A - T_N) \times N_{\text{Thio}} \times 24.04 \times 10^6}{4000 \times S_C \times t_S} \\ &= \frac{6010 (T_A - T_N) \times N_{\text{Thio}}}{S_C \times t_S} \end{aligned}$$

where, in Equations 3, 4, 5, 6, and 7:

t_S = Time sampled, minutes.

T_N = Neutral titer, mL

T_A = Acid titer (total), mL

N_{Thio} = Normality of sodium thiosulfate titrant

2.7 Alternative procedures - Not applicable to this method.

2.8 References

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2.9 Tables, diagrams, flowcharts, and validation data

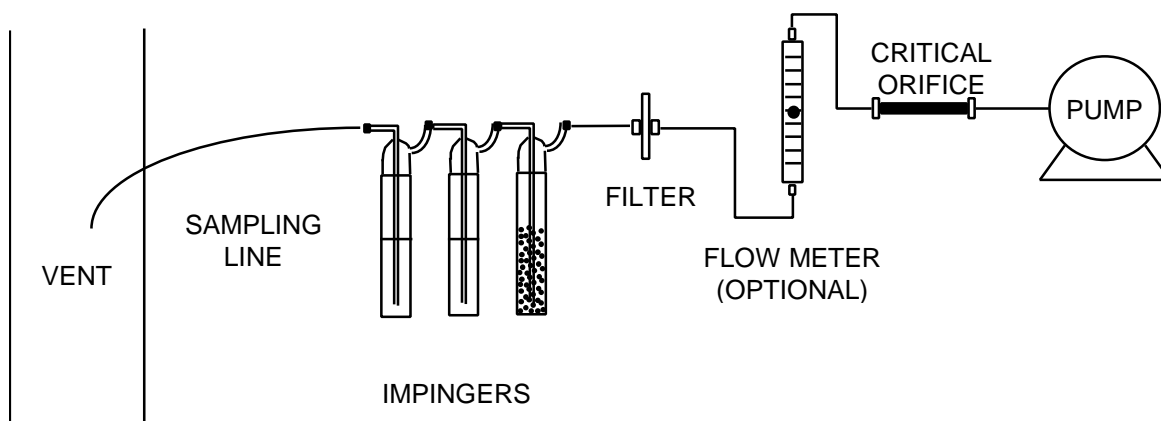


Figure 1. Sampling Train