

## METHOD 200

### DETERMINATION OF TOTAL PARTICULATE, FREE CHLORINE, AND TOTAL CHLORIDES FROM SECONDARY ALUMINUM SMELTERS AND OTHER STATIONARY SOURCES

#### 1. Applicability and Principle

1.1 Applicability. This method applies to the determination of total particulate, free chlorine, and total chloride emissions in secondary aluminum production facilities and in other sources when specified in the regulations.

1.2 Principle. Total particulate, free chlorine, and total chloride emissions are withdrawn isokinetically from the source using a modified EPA Method 5 procedure. The total particulate and any particulate chlorides present are collected on the glass fiber filter maintained at a temperature not to exceed 93°C (200°F); free chlorine and the remaining chlorides are collected in a 0.1 N KOH impinger solution. The particulate mass is determined gravimetrically after removal of combined water. Free chlorine is measured in the impinger catch using the DPD Ferrous Titrimetric Method<sup>(1)</sup>.

#### 2. Range

2.1 For Determination of Total Free Chlorine by the DPD Ferrous Titrimetric Method. The minimum chlorine concentration detectable by this method has not been determined. The maximum for which this method is suitable, as described here, is 4 mg/L. Where the total available chlorine exceeds 4 mg/L, a smaller sample, diluted to a total volume of 100 ml, should be used.

2.2 For Determination of Total Chloride by the Mercuric Nitrate Method. The mercuric nitrate method can be used to measure total chloride when the sample to be titrated contains 0.15 to 10 mg Cl. For illustrative purposes, a 10 ml sample containing 0.15 mg Cl would be equivalent to a concentration of 15 mg/L, and a 10 ml sample containing 10 mg Cl would be equivalent to a concentration of 1000 mg/L. Depending upon the type of sample, the quantity in the portion to be titrated could be adjusted to the measurable range by dilution or by evaporation of excess liquid.

#### 3. Interferences

3.1 For Determination of Total Chlorine by the DPD Ferrous Titrimetric Method. The only interferences for this method are copper and oxidized manganese. Interferences by copper up to approximately 10 mg/L is overcome by the EDTA (ethylenediamine tetraacetate dihydrate) incorporated in the reagents. A suitable correction for interference due to oxidized manganese is provided in Reference 1. It is not included here because oxidized manganese is not expected to occur in samples from secondary aluminum smelters in high enough concentrations to cause significant interference. The interference of combined chlorine is insignificant in the determination of free chlorine except at high temperature and long waiting times.

This method has been adapted from a standard method for the measurement of chlorine in water. In such cases, ammonia and certain nitrogenous compounds are often present which can combine with the free chlorine to form chloramines. While it is unlikely that such compounds will be encountered in analyses of samples of aluminum smelter stack effluents, the potential interference which could be caused by such compounds and the procedure for compensation for this interference are discussed in Reference 1.

3.2 For Determination of Total Chloride by the Mercuric Nitrate Method. Bromide and iodide are

titrated with mercuric nitrate in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in excess of 10 ml/L. These should not present a problem in samples from a secondary aluminum smelter.

Where metal ion interference is expected, its presence can be established by passing a sample aliquot through an ion exchange column of Rexyn 101H. This procedure may also be used to eliminate such interference. The presence of these ions is not expected in secondary aluminum reverberatory furnace exhaust gases except where the air pollution control scrubber uses low quality water, and there is a droplet carryover.

#### 4. Precision, Accuracy, and Stability

##### 4.1 Precision and Accuracy.

4.1.1 For Determination of Total Free Chlorine by the DPD Ferrous Titrimetric Method. The precision and accuracy of the method, and several other methods for chlorine analysis, were studied under the auspices of the American Public Health Association, the American Water Works Association, and the Water Pollution Federation. A more detailed discussion of the study may be found in Reference 3. Briefly, samples of known concentrations of free and combined chlorine were distributed to 15 to 30 participating laboratories for analysis. The results of the two studies are summarized in Reference 1. Sample concentrations for Study No. 2 were:

Sample No. 1, 440  $\mu\text{g/L}$  free chlorine;  
Sample No. 2, 980  $\mu\text{g/L}$  free chlorine; and  
Sample No. 3, 660  $\mu\text{g/L}$  combined chlorine.

The DPD Ferrous Titrimetric Method was one of the more accurate and precise of those tested. Data presented in Reference 1 attribute a relative standard deviation of 39.8% for results of 19 different laboratory analyses for 0.8 mg/L  $\text{Cl}_2$  by the DPD Ferrous Titrimetric Method.

4.1.2 For Determination of Total Chloride by the Mercuric Nitrate Method. A synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrite N, 259 mg/L sulfate, and 42.5 mg/L total alkalinity (contributed by  $\text{NaHCO}_3$ ) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3%, and a relative error of 2.9%.

##### 4.2 Stability.

4.2.1 For Determination of Total Free Chlorine by the DPD Ferrous Titrimetric Method. Samples containing free chlorine are relatively unstable and cannot be stored. Further, exposure of samples to strong light or agitation will accelerate reduction of their chlorine content. Therefore, chlorine analyses must be completed on-site within two hours of sample collection, avoiding excessive light and agitation.

4.2.2 For Determination of Total Chloride by the Mercuric Nitrate Method. Samples containing total chloride are sufficiently stable to be returned to the laboratory for analysis.

#### 5. Apparatus

5.1 Sampling Train. The schematic diagram of the sampling train in Figure 1 shows that it is similar in construction to the Method 5 train. Apparatus is the same as Method 5, Sections 2.1.1, 2.1.2, 2.1.3, 2.1.4, 2.1.5, 2.1.8, 2.1.9, and 2.1.10.

5.1.1 Filter Heating System. Should be capable of maintaining the temperature around the filter

up to but not exceeding 93°C.

5.1.2 Condenser/Impingers. Same as Method 5, Section 2.1.7, except the first three impingers will each be charged with 100 ml of 0.1 N potassium hydroxide (KOH) in chlorine-demand-free water. An empty impinger will not be used.

5.2 Sample Recovery. Same as Method 5, Section 2.2, except all washing will be done with chlorine-demand-free water, and no acetone will be used.

5.3 Analysis. Same as Method 5, Section 2.3, adding the following:

5.3.1 Beakers. 1000 ml.

5.3.2 Pipettes. Volumetric type 1-, 5-, 10-, 15-, 20-, and 25-ml sizes.

5.3.3 Burettes. 10- and 25-ml sizes.

5.3.4 Graduated Cylinder. 500-ml, graduated in divisions of 2 ml, capable of measuring volume to  $\pm 1$  ml.

5.3.5 Thermometer. 0-100°C.

5.3.6 Volumetric Flasks. 50-, 100-, 200-, and 250-ml sizes.

5.3.7 Analytical balance capable of weighing to 0.1 mg.

5.3.8 Petri dishes for filter storage.

5.3.9 pH meter with non-chloride reference electrode and/or pH indicator tape.

## 6. Reagents<sup>1</sup>

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 Sampling and Sample Recovery. The reagents used in sample recovery are as follows:

6.1.1 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 3.1.2, 3.1.4, and 3.1.5.

6.1.2 Water, Deionized/Distilled, Chlorine-Demand-Free. Chlorine-demand-free deionized/distilled water (DDCDF) will be used for all sampling, sample recovery, and analysis. A minimum of 20 liters should be prepared for a sample series. To prepare chlorine-demand-free water, add sufficient chlorine to deionized/distilled water to destroy ammonia, other nitrogen compounds, and organic material. The resultant chlorine excess (residual) can be reduced by addition of sodium thiosulfate. It is preferable to ere on the side of excess chlorine rather than chlorine demand, as the chlorine content can be subtracted as a blank. Using the DPD Ferrous Titrimetric Method or other chlorine measurement methods specified in Standard Methods for Examination of Water and Wastewater, a chlorine residual, of less than 0.05 mg/liter should be achieved.

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<sup>1</sup>Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

Hack Chemical Company of Ames, Iowa manufactures a simplified chlorine detection apparatus that detects chlorine at 5.0 nanograms per liter. By slowly adding chlorine to deionized/distilled water and stirring to assist reaction, a slight chlorine excess can be achieved and the addition of sodium thiosulfate to reduce chlorine may not be necessary. In either of these methods, sufficient time and mixing should be allowed for the chlorine demand to react with added chlorine. Chlorine-demand-free water can also be prepared by Ion Exchange as described in Method 4096 of Reference 1.

Chlorine-demand-free water should be stored in glass containers, and displacement air passing into the container should pass through a charcoal filter.

6.1.3 Potassium Hydroxide, 0.1 N. Dissolve 5.6 g KOH in 800 ml of DDCDF water in a 1-liter flask, and dilute to exactly 1000 ml with DDCDF water.

6.2 Analysis. The reagents needed for analysis are listed below:

6.2.1 For Determination of Free Chlorine by the DPD Ferrous Titrimetric Method.

6.2.1.1 Water, Deionized/Distilled, Chlorine-Demand-Free. Same as in Section 6.1.2.

6.2.1.2 Phosphate Buffer Solution. Dissolve 24 g anhydrous disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , and 46 g anhydrous potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , in DDCDF water. Combine with 100 ml DDCDF water in which 0.800 mg disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetic acid sodium salt, have been dissolved. Dilute to 1 L with DDCDF water and add 0.020 mg  $\text{HgCl}_2$  to prevent mold growth and to prevent interference in the free available chlorine test caused by any trace amounts of iodide in the reagents.

6.2.1.3 N, N-Diethyl-p-phenylenediamine (DPD) Indicator Solution. Dissolve 1 g DPD Oxalate<sup>2</sup>, or 1.5 g p-amino-N:N-diethylaniline sulfate<sup>3</sup>, in DDCDF water containing 8 ml 1+3  $\text{H}_2\text{SO}_4$ <sup>4</sup> and 0.200 g disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) tetraacetate acid sodium salt. Make up to 1 L, store in a brown glass-stoppered bottle, and discard when discolored. (The buffer and indicator sulfate are commercially available as a combined reagent in stable powder form.)

**CAUTION:** The oxalate is toxic -- take care to avoid ingestion.

6.2.1.4 Standard Ferrous Ammonium Sulfate (FAS) Titrant. Dissolve 1.106 g Mohr's salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in DDCDF water containing 1 ml of 1+3  $\text{H}_2\text{SO}_4$  and make up to 1 L with freshly boiled and cooled distilled water. This primary standard may be used for 1 month, and the titer checked daily by potassium dichromate. (See Section 8, Calibrations). The FAS titrant is equivalent to 100  $\mu\text{g}$  Cl/1.00 ml.

6.2.1.5 1+3 Sulfuric Acid Solution. Cautiously add 250 ml concentrated  $\text{H}_2\text{SO}_4$  to 600 ml DDCDF water and dilute to 1 L (i.e., 1 part concentrated  $\text{H}_2\text{SO}_4$  + 3 parts DDCDF water).

6.2.1.6 Potassium Iodide (KI). Crystals of KI.

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<sup>2</sup>Eastman chemical No. 7102, or equivalent.

<sup>3</sup>British Drug House chemical available from Gallard-Schlesinger Chemical Mfg. Corp., 584 Mineola Avenue, Carle Place, N.Y. 11514.

<sup>4</sup>See paragraph 6.2.1.5 of this section.

6.2.1.7 Hydrogen Peroxide. 3 percent solution.

6.2.1.8 Potassium Dichromate. Crystals of  $K_2Cr_2O_7$ .

6.2.1.9 Ferroin Indicator.

6.2.2 For Determination of Total Chloride by the Mercuric Nitrate Method.

6.2.2.1 Water. Deionized distilled. Not necessary to be chlorine-demand-free.

6.2.2.2 Standard Sodium Chloride, 0.0100 N. Dissolve 0.584 g NaCl (dried at 140°C) in deionized/distilled water and dilute to 1 L.

6.2.2.3 Nitric Acid,  $HNO_3$ , 0.1 N. Dilute 3.2 ml concentrated  $HNO_3$  (69%) to 500 ml with deionized/distilled water.

6.2.2.4 Sodium Hydroxide, NaOH, 0.1 N. Dissolve 2 g NaOH in deionized/distilled water and dilute to 500 ml.

6.2.2.5 Reagents for Low Chloride Titrations.

6.2.2.5.1 Indicator Reagent. Dissolve, in the order named, 0.250 g s-diphenylcarbazone, 4 ml of concentrated nitric acid, and 0.030 g xylene cyanol FF in 100 ml 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow end point and high results.

6.2.2.5.2 Standard Mercuric Nitric Titrant, Approximately 0.0141 N. Dissolve 2.3 g  $Hg(NO_3)_2$  or 2.5 g  $Hg(NO_3)_2 \cdot H_2O$  in 100 ml deionized/distilled water. Dilute to just under 1 L. The  $Hg(NO_3)_2$  titrant is equal to approximately 0.50 mg Cl/ml. (See Section 8 for calibrations).

6.2.2.6 Reagents for High-Chloride Titrations.

6.2.2.6.1 Mixed Indicator Reagent. Dissolve 5 g diphenylcarbazone powder and 0.5 g bromphenol blue powder in 750 ml 95% ethyl or 100% isopropyl alcohol and dilute to 1 L with ethyl or isopropyl alcohol.

6.2.2.6.2 Strong Standard Mercuric Nitrate Titrant, 0.141 N. Dissolve 23 g  $Hg(NO_3)_2$  or 25 g  $Hg(NO_3)_2 \cdot H_2O$  in 900 ml deionized/distilled water containing 5.0 ml conc.  $HNO_3$ . Dilute to just under 1 L.

6.2.3 For Determination of Total Water Soluble Particulate Chloride by the Mercuric Nitrate Method.

6.2.3.1 Water. Deionized/distilled.

6.2.3.2 Other reagents same as in Sections 6.2.2.2 through 6.2.2.6, since samples are to be analyzed by the mercuric nitrate method.

## 7. Procedure

7.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedure to ensure reliable results.

7.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 4.1.1.

7.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 4.1.2, except as follows: Select a nozzle size based on the range of velocity heads in order to maintain isokinetic rates below 28 liters/min. (1.0 cfm).

7.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 4.1.3, except place 100 ml of 0.1 N potassium hydroxide in each of the first three impingers, and place the preweighed silica gel in the fourth impinger. Assemble the train as shown in Figure 1.

7.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

7.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2. Maintain isokinetic sampling rates less than 28 liters/min. (1.0 cfm). Maintain filter and probe temperatures at a minimum of 10°C above stack temperature, but no higher than 93°C.

7.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

7.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while sampling train is cooling down. Capping would create a vacuum and thus draw water from the impingers into the probe.

Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the filter and the probe disconnect the line at the probe and let any condensed water or liquid drain into the impingers or condenser. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe-filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind to minimize the chances of contaminating or losing the sample.

7.2.1 Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edge blade. Seal the container.

Container No. 2. Probe Nozzle, Probe Fitting, Probe Liner, and Front-half of Filter Holder. Taking care to see that dust on the outside of the probe or other exterior surfaces do not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front-half of the filter holder by washing these components with deionized/distilled chlorine-demand-free (DDCDF) water and placing the wash in a glass container. Save a water blank for analysis. Perform the rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with DDCDF water from a wash bottle and brushing with a Nylon bristle brush. Brush until the water rinse shows no visible particles, after which make a final rinse of the inside surface with DDCDF water.

Brush and rinse the inside parts of the Swagelok fitting with DDCDF water in a similar way until no visible particles remain.

Rinse the probe liner with DDCDF water by tilting and rotating the probe while squirting DDCDF water into its upper end so that all inside surfaces will be wetter with DDCDF water. Let the deionized/distilled water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the DDCDF water rinse with a probe brush. Hold the probe in an inclined position, squirt DDCDF water into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any DDCDF water and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the DDCDF water or until none remains in the probe liner on visual inspection. Rinse the brush with DDCDF water, and quantitatively collect these washings in the sample container. After the brushing, make a final DDCDF water rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with Nylon bristle brush and rinsing with DDCDF water. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone also (if applicable). After all DDCDF water washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that DDCDF water will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. Silica Gel. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

Container No. 4. Impinger Solution and Back-Half Wash. Treat the first three impingers as follows: leaving each impinger intact to transfer the liquid, cap off the inlet, and pour the liquid through the outlet into a graduated cylinder or directly into a tared sample container. Record the volume to within  $\pm 0.5$  g. Transfer the liquid to the sample container. Next, rinse surfaces of the first three impingers and the glass connecting joints with DDCDF water. Use rinse water sparingly to avoid excessive dilution of the sample. A Nylon bristle brush may be used to facilitate removal of any adhering material.

After transferring the impinger solution and back-half wash to the sample container, tighten the lid on the sample container so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine later whether leakage occurred during transport. Label the container to clearly identify its contents.

"Water-Blank" Container - Fill a 200-ml container with DDCDF water taken from the same source as that used for washing of the sampling train.

"KOH Collecting Solution Blank" Container - Fill a 500-ml container with KOH collecting solution taken from the same batch as that used in the impingers.

"Filter Blank" - Take a tared unused filter from the field supply for transfer to the laboratory for

analysis.

### 7.3 Analysis.

Container No. 1 - Filter. Same as in Method 5, Section 4.2 except change temperature in oven drying option to 90°C. Also after completion of the filter gravimetric analysis, extract water soluble chloride from the filter by macerating in 100 ml of deionized/distilled water with a glass stirring rod. Determine total chloride by the Mercuric Nitrate Method (Section 7.3.2). Chloride determination of the filter extract can be conducted separately from the impinger solution and back-half wash, which would allow the latter to be analyzed without waiting for filter desiccation; or can be combined for analysis with the impinger solution and wash.

Container No. 2 - Probe and Front-half Wash. Transfer to appropriately sized volumetric flask. Dilute to the mark with deionized/distilled water. With a pipette, take exactly 50 ml for chloride titration, and dry-down the remainder for total particulate determination.

Container No. 4 - Impinger Solution and Back-half Wash. Bring to 500 ml volume. Pipette a 100 ml aliquot for free chlorine analysis. This should be conducted within two hours of test completion. The remaining 400 ml of solution will be returned to the laboratory for total chloride analysis.

"Water Blank" Container - Measure deionized/distilled water in this container either volumetrically or gravimetrically. Transfer the deionized/distilled water to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

**NOTE:** At the option of the tester, the contents of Container No. 2 as well as the deionized/distilled water blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point; also, to prevent "bumping", the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature.

"KOH Collecting Solution Blank" Container - Methods for determination of blank values to be used in chlorine and total chloride analysis are described in the following Section 7.3.1 and 7.3.2.

"Filter Blank" - Analyze in identical manner as that conducted on the Container No. 1 filter.

7.3.1 Determination of Total Free Chlorine by the DPD Ferrous Titrimetric Method. This method has been adapted from a standard method for water analysis. Thus, sample conditions often encountered in water analysis but not likely in analyses of stack samples, are not discussed. On the other hand, sample conditions for stack effluent analyses which are different from those encountered in water analyses, must be taken into account.

Careful pH control is essential for accurate results with this method. As received for analysis, the sample may be strongly alkaline. Further, the titration must be carried out at a pH of 6.2 to 6.5 to produce a sharp colorless endpoint, and accurate measurement of free chlorine. The pH of the sample must, therefore, be checked prior to analysis and reduced, if necessary.

From the 100 ml aliquot of the impinger solution and back-half wash withdrawn from Container No. 3 (paragraph 7.3) for free chlorine analysis, treat a small measured test sample with determined quantities of 1 + 3 sulfuric acid solution (Section 6.2.1.5) till the pH has been reduced to 7.5 to 8. Test for pH with pH paper or a reference electrode. With the quantity of acid known to reduce the test sample pH to 7.5 to 8, ratio this amount to the amount required to achieve the same pH range in a separate exact 25 ml sample. After reducing the 25 ml sample pH, add deionized/distilled water to bring the volume of



this sample up to exactly 100 ml.

To determine total available chlorine (i.e., total free and combined available chlorine), place 5 ml each of buffer reagent and DPD indicator solution in a 250 ml titration flask and mix (or use about 500 mg of DPD powder). Add the 100 ml sample and mix.

To liberate combined chlorine, should any be present (i.e., as chloramine or nitrogen trichloride), add several crystals of KI (about 1/2 to 1 g) and mix to dissolve. Let stand for 2 minutes and titrate rapidly with standard FAS titrant until the red color is discharged. Record the volume of titrant used as reading A. If color driftback indicates slightly incomplete reaction, let stand 2 minutes and titrate until the red color is again discharged. Record the quantity of titrant used and add to reading A.

Determine the blank by titrating 100 ml of KOH collecting solution in the same manner as above, making sure all pH adjustments are correctly made.

**Explanatory Notes:** The quantities given above are suitable for concentrations of total available chlorine up to 4 mg/L. Where the total chlorine exceeds 4 mg/L, use a smaller sample and dilute to a total volume of 100 ml. Mix the usual volumes of buffer reagent and DPD indicator solution, or the usual amount of DPD powder, with deionized/distilled water before adding sufficient sample to bring the total volume to 100 ml.

Too high a pH may cause dissolved oxygen to give a color.

**Compensation for Interferences:** Should the presence of oxidized manganese be found or suspected, the interference can be corrected by placing 5 ml of buffer solution, one small crystal of potassium iodide, and 0.5 ml sodium arsenite solution (500 mg NaAsO<sub>2</sub> plus 100 ml distilled water) in the titration flask. Add 100 ml sample and mix. Add 5 ml DPD indicator solution, mix, and titrate with standard ferrous ammonium sulfate titrant until any red color is discharged. Subtract the reading from reading A. If the combined reagent in powder form is used, add the potassium iodide and arsenite first to the sample and mix, then add the combined buffer-indicator reagent afterwards.

**7.3.2 Determination of Total Chloride by the Mercuric Nitrate Method.** When using the mercuric nitrate method to determine total chloride, it is necessary to pretreat any impinger sample aliquot with hydrogen peroxide in order to destroy any residual chlorine remaining in the sample. Residual chlorine gradually decomposes to form chlorides, so in order to eliminate questions concerning the percentage conversion, all field samples will require the pretreatment. After a total chloride has been determined, that portion contributed by the chlorine will have to be subtracted (i.e., two times the chlorine concentration). Thus, in order to convert any free chlorine to hypochlorite to chloride, add to the collected sample 2 ml of 3 percent hydrogen peroxide solution per 100 ml of sample and mix.

Because pH control is critical in this method, adjust the pH of each sample to  $2.5 \pm 0.1$  with 0.1 N HNO<sub>3</sub> or NaOH before titrating. Use a pH meter with nonchloride type of reference electrode for the pH adjustment. If only the usual chloride type reference electrode is available for pH adjustment, determine the amount of acid or alkali required to achieve a pH of  $2.5 \pm 0.1$  and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue the analysis to its prescribed end. If no pH meter is available, make the necessary adjustments using pH indicator paper.

**7.3.2.1 Titration of Low Chloride Concentrations.** Use a 100 ml sample or smaller portion so that the chloride content is less than 10 mg.

Add 1.0 ml of indicator reagent to the sample. (The color of the solution should be green-blue at this point. A light green indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8).

Titrate the treated sample with 0.0141 N mercuric nitrate titrant to a definite purple end point. The solution will turn from green-blue to blue a few drops from the end point.

Determine the blank by titrating 100 ml of KOH collecting solution.

**Explanatory Note:** Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the end point of this titration by formation of a purple complex with the excess mercuric ions. The error in titration is about 1% of the volume of titrant used per change of 0.1 pH unit in the pH range 2.1 to 2.8. If exact pH adjustment is not possible because no pH meter is available, it is felt that keeping within a range of  $\pm 0.1$  pH unit using pH paper is sufficient for most analyses. In the low chloride procedure, the alcohol solution of diphenylcarbazone also contains xylene cyanol FF which is used as a pH indicator and as a background color to facilitate end-point detection. Increasing the strength of the titrant and modifying the indicator mixture enable determination of higher chloride concentrations.

**7.3.2.2 Titration of High Chloride Concentrations.** Place 50.0 ml sample in a 150-ml beaker (5.00 ml sample may be used when more than 5 ml titrant is needed). Add approximately 0.5 ml mixed indicator reagent and mix well. The color should be purple. Add 0.1 N HNO<sub>3</sub> dropwise until the color just turns yellow. Titrate with 0.141 N mercuric nitrate titrant to the first permanent dark purple. Titrate a 50 ml volume of KOH collecting solution as a blank using the sample procedure.

## 8. Calibrations

**8.1 Sampling Train.** Sampling train calibrations are the same as EPA Method 5, Section 5.

**8.2 Standard Ferrous Ammonium Sulfate (FAS) Titrant (for DPD Ferrous Titrimetric Method).** Prepare 0.025 N standard potassium dichromate (4) solution by dissolving 1.226 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, ACS reagent grade or equivalent, previously dried at 103°C for 2 hours, in distilled water and dilute to 1000 ml. For standardizing the FAS titrant (Section 6.2.1.4), dilute 1.0 ml standard K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to about 25 ml. Add 3 ml concentrated H<sub>2</sub>SO<sub>4</sub> and cool. Titrate with the ferrous ammonium sulfate titrant, using 2 to 3 drops (0.10 to 0.15 ml) ferroin indicator.

$$\text{Normality of FAS} = \frac{\text{ml } K_2Cr_2O_7 \times 0.025}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

Prepare ferroin indicator solution by dissolving 1.485 g 1,10-phenanthroline monohydrate, together with 695 mg FeSO<sub>4</sub> · 7H<sub>2</sub>O in water and dilute 100 ml. This indicator solution may be purchased already prepared.

**8.3 Standard Mercuric Nitrate Titrant (For Mercuric Nitrate Method).** Prepare 0.0141 N standard sodium chloride solution by dissolving 8.243 g NaCl dried at 105°C in distilled water and dilute to 500 ml. Dilute 50 ml of the standard sodium chloride solution to 1000 ml; 1.00 ml equals 0.500 mg following the titration procedure described in Section 7.3.2.1 Use replicates containing 5.00 ml standard NaCl solution diluted to 100 ml with deionized distilled water. Store the Hg(NO<sub>3</sub>)<sub>2</sub> titrant away from the light in a dark bottle.

**8.4 Strong Standard Mercuric Nitrate Titrant (For Mercuric Nitrate Method).** Using 0.0141 standard sodium chloride solution from 8.3, perform a preliminary standardization by following the titration procedure described in 7.3.2.2. Use replicates containing 25 ml standard NaCl solution and 25 ml deionized distilled water. The chloride equivalence of the titrant is approximately 5 mg/ml. Store the Hg(NO<sub>3</sub>)<sub>2</sub> titrant away from the light in a dark bottle.

9. Calculations

9.1 Calculations for Total Particulate are the same as Method 5, Section 6.

9.2 For Determination of Total Free Chlorine by the DPD Ferrous Titrimetric Method. Use the following equation to calculate the total mass in the sample volume.

$$M_s = \left[ \frac{(V_{TA} - V_{TB}) V_s (N) 35.45 (2)}{V_a} \right]$$

Where:

- $M_s$  = total mass chlorine in the sample (mg)
- $V_{TA}$  = volume of titer for aliquot (ml)
- $V_{TB}$  = volume of titer for blank (ml)
- $V_s$  = volume of sample used for analysis (500 ml for this procedure)
- $N$  = normality of ferrous ammonium sulfate titer (as described in this method is

$$N = \frac{1.106 \text{ g } Fe(NH_4)_2(SO_4)_2}{392.15 \text{ g/molar equivalent}} = 0.00282$$

- 35.45 = molecular weight of chlorine
- $V_a$  = volume of aliquot used for analyses, ml (25 ml for this procedure)
- 2 = only one of the two chlorine atoms is available for titration

9.3 For Determination of Total Chloride by the Mercuric Nitrate Method. Calculation of total chloride in collected samples is accomplished as follows:

$$M_s = \frac{(V_{TB} - V_{BA}) V_s (N) 35.45}{V_a}$$

Where:

- $M_s$  = mass chloride in sample (mg)
- $V_{TA}$  = volume of titer for aliquot (ml)
- $V_{BA}$  = volume of titer for blank aliquot (ml)
- $V_s$  = volume of sample (ml)
- $N$  = normality of Mercuric Nitrate (by the method is 0.1449)
- 35.45 = molecular weight of chlorine
- $V_a$  = volume of aliquot (ml)

10. Bibliography

1. Standard Methods for Examination of Water and Wastewater, American Public Health Association, 1975, pp.
2. Ibid. pp.
3. Ibid. pp.
4. Ibid. pp.