

## 4500-Cl G. DPD Colorimetric Method

## 1. General Discussion

*a. Principle:* This is a colorimetric version of the DPD method and is based on the same principles. Instead of titration with standard ferrous ammonium sulfate (FAS) solution as in the titrimetric method, a colorimetric procedure is used.

*b. Interference:* See 4500-Cl.A.3 and F.1*d*. Compensate for color and turbidity by using sample to zero photometer. Minimize chromate interference by using the thioacetamide blank correction.

*c. Minimum detectable concentration:* Approximately 10 µg Cl as Cl<sub>2</sub>/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.

*d. Quality control (QC):* The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

## 2. Apparatus

*a. Photometric equipment:* One of the following is required:

1) *Spectrophotometer*, for use at a wavelength of 515 nm and providing a light path of 1 cm or longer.

2) *Filter photometer*, equipped with a filter having maximum transmission in the wavelength range of 490 to 530 nm and providing a light path of 1 cm or longer.

*b. Glassware:* Use separate glassware, including separate spectrophotometer cells, for free and combined (dichloramine) measurements, to avoid iodide contamination in free chlorine measurement.

## 3. Reagents

See 4500-Cl.F.2*a*, *b*, *c*, *d*, *e*, *h*, *i*, and *j*.

## 4. Procedure

*a. Calibration of photometric equipment:* Calibrate instrument with chlorine or potassium permanganate solutions.

1) *Chlorine solutions*—Prepare chlorine standards in the range of 0.05 to 4 mg/L from about 100 mg/L chlorine water standardized as follows: Place 2 mL acetic acid and 10 to 25 mL chlorine-demand-free water in a flask. Add about 1 g KI. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL 0.025*N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titrant (see 4500-Cl.B.2*d*) is equivalent to about 0.9 mg chlorine. Titrate with standardized 0.025*N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titrant until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to disappearance of blue color.

Determine the blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for titration. Perform blank titration A or B, whichever applies, according to 4500-Cl.B.3*d*.

$$\text{mg Cl as Cl}_2/\text{mL} = \frac{(A + B) \times N \times 35.45}{\text{mL sample}}$$

where:

*A* = mL titrant for sample,

*B* = mL titrant for blank (to be added or subtracted according to required blank titration. See 4500-Cl.B.3*d*), and

*N* = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

Use chlorine-demand-free water and glassware to prepare these standards. Develop color by first placing 5 mL phosphate buffer solution and 5 mL DPD indicator reagent in flask and then adding 100 mL chlorine standard with thorough mixing as described in ¶s *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with standard FAS titrant as a check on chlorine concentration.

2) *Potassium permanganate solutions*—Prepare a stock solution containing 891 mg KMnO<sub>4</sub>/1000 mL. Dilute 10.00 mL stock solution to 100 mL with distilled water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with distilled water, a chlorine equivalent of 1.00 mg/L will be produced in the DPD reaction. Prepare a series of KMnO<sub>4</sub> standards covering the chlorine equivalent range of 0.05 to 4 mg/L. Develop color by first placing 5 mL phosphate buffer and 5 mL DPD indicator reagent in flask and adding 100 mL standard with thorough mixing as described in ¶s *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with FAS titrant as a check on any absorption of permanganate by distilled water.

Obtain all readings by comparison to color standards or the standard curve before use in calculation.

*b. Volume of sample:* Use a sample volume appropriate to the photometer or colorimeter. The following procedure is based on using 10-mL volumes; adjust reagent quantities proportionately for other sample volumes. Dilute sample with chlorine-demand-free water when total chlorine exceeds 4 mg/L.

*c. Free chlorine:* Place 0.5 mL each of buffer reagent and DPD indicator reagent in a test tube or photometer cell. Add 10 mL sample and mix. Read color immediately (Reading *A*).

*d. Monochloramine:* Continue by adding one very small crystal of KI (about 0.1 mg) and mix. If dichloramine concentration is expected to be high, instead of small crystal add 0.1 mL (2 drops) freshly prepared KI solution (0.1 g/100 mL). Read color immediately (Reading *B*).

*e. Dichloramine:* Continue by adding several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color (Reading *C*).

*f. Nitrogen trichloride:* Place a very small crystal of KI (about 0.1 mg) in a clean test tube or photometer cell. Add 10 mL sample and mix. To a second tube or cell add 0.5 mL each of buffer and indicator reagents; mix. Add contents to first tube or cell and mix. Read color immediately (Reading *N*).

*g. Chromate correction using thioacetamide:* Add 0.5 mL thioacetamide solution (F.2*i*) to 100 mL sample. After mixing, add buffer and DPD reagent. Read color immediately. Add several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color. Subtract the first reading from Reading *A* and the second reading from Reading *C* and use in calculations.

*h. Simplified procedure for total chlorine:* Omit Step *d* above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add the full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator. Read color after 2 min.

## 5. Calculation

Reading	NCl <sub>3</sub> Absent	NCl <sub>3</sub> Present
A	Free Cl	Free Cl
B - A	NH <sub>2</sub> Cl	NH <sub>2</sub> Cl
C - B	NHCl <sub>2</sub>	NHCl <sub>2</sub> + ½NCl <sub>3</sub>
N	—	Free Cl + ½NCl <sub>3</sub>
2(N - A)	—	NCl <sub>3</sub>
C - N	—	NHCl <sub>2</sub>

In the event that monochloramine is present with NCl<sub>3</sub>, it will be included in Reading N, in which case obtain NCl<sub>3</sub> from 2(N - B).

## 6. Bibliography

See 4500-Cl.F.6.

## 4500-Cl H. Syringaldazine (FACTS) Method

## 1. General Discussion

*a. Principle:* The free (available) chlorine test, syringaldazine (FACTS) measures free chlorine over the range of 0.1 to 10 mg/L. A saturated solution of syringaldazine (3,5-dimethoxy-4-hydroxybenzaldazine) in 2-propanol is used. Syringaldazine is oxidized by free chlorine on a 1:1 molar basis to produce a colored product with an absorption maximum of 530 nm. The color product is only slightly soluble in water; therefore, at chlorine concentrations greater than 1 mg/L, the final reaction mixture must contain 2-propanol to prevent product precipitation and color fading.

The optimum color and solubility (minimum fading) are obtained in a solution having a pH between 6.5 and 6.8. At a pH <6, color development is slow and reproducibility is poor. At a pH >7, the color develops rapidly but fades quickly. A buffer is required to maintain the reaction mixture pH at approximately 6.7. Take care with waters of high acidity or alkalinity to assure that the added buffer maintains the proper pH.

Temperature has a minimal effect on the color reaction. The maximum error observed at temperature extremes of 5 and 35°C is ±10%.

*b. Interferences:* Interferences common to other methods for determining free chlorine do not affect the FACTS procedure. Monochloramine concentrations up to 18 mg/L, dichloramine concentrations up to 10 mg/L, and manganese concentrations (oxidized forms) up to 1 mg/L do not interfere. Trichloramine at levels above 0.6 mg/L produces an apparent free chlorine reaction. Very high concentrations of monochloramine (≥35 mg/L) and oxidized manganese (≥2.6 mg/L) produce a color with syringaldazine slowly. Ferric iron can react with syringaldazine; however, concentrations up to 10 mg/L do not interfere. Nitrite (≤250 mg/L), nitrate (≤100 mg/L), sulfate (≤1000 mg/L), and chloride (≤1000 mg/L) do not interfere. Waters with high hardness (≥500 mg/L) will produce a cloudy solution that can be compensated for by using a blank. Oxygen does not interfere.

Other strong oxidizing agents, such as iodine, bromine, and ozone, will produce a color.

*c. Minimum detectable concentration:* The FACTS procedure is sensitive to free chlorine concentrations of 0.1 mg/L or less.

*d. Quality control (QC):* The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

## 2. Apparatus

*Colorimetric equipment:* One of the following is required:

*a. Filter photometer,* providing a light path of 1 cm for chlorine concentrations ≤1 mg/L or a light path from 1 to 10 mm for chlorine concentrations above 1 mg/L; also equipped with a filter having a band pass of 500 to 560 nm.

*b. Spectrophotometer,* for use at 530 nm, providing the light paths noted above.

## 3. Reagents

*a. Chlorine-demand-free water:* See 4500-Cl.C.3m. Use to prepare reagent solutions and sample dilutions.

*b. Syringaldazine indicator:* Dissolve 115 mg 3,5-dimethoxy-4-hydroxybenzaldazine\* in 1 L 2-propanol.

*c. 2-Propanol:* To aid in dissolution use ultrasonic agitation or gentle heating and stirring. Redistill reagent-grade 2-propanol to remove chlorine demand. Use a 30.5-cm Vigreux column and take the middle 75% fraction. Alternatively, chlorinate good-quality 2-propanol to maintain a free residual overnight; then expose to UV light or sunlight to dechlorinate. **CAUTION: 2-Propanol is extremely flammable.**

*d. Buffer:* Dissolve 17.01 g KH<sub>2</sub>PO<sub>4</sub> in 250 mL water; pH should be 4.4. Dissolve 17.75 g Na<sub>2</sub>HPO<sub>4</sub> in 250 mL water; the pH should be 9.9. Mix equal volumes of these solutions to obtain FACTS buffer, pH 6.6. Verify pH with pH meter. For waters containing considerable hardness or high alkalinity other pH 6.6 buffers can be used, for example, 23.21 g maleic acid and 16.5 mL 50% NaOH per liter of water.

*e. Hypochlorite solution:* Dilute household hypochlorite solution, which contains about 30 000 to 50 000 mg Cl equivalent/L, to a strength between 100 and 1000 mg/L. Standardize as directed in 4500-Cl.G.4a1).

## 4. Procedure

*a. Calibration of photometer:* Prepare a calibration curve by making dilutions of a standardized hypochlorite solution

\* Aldrich No. 17, 753-9, Aldrich Chemical Company, Inc., 1001 West St. Paul Ave., Milwaukee, WI 53233, or equivalent.